

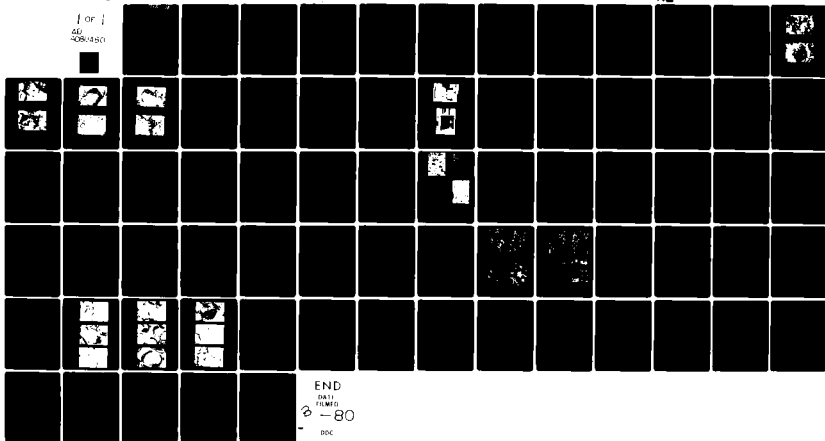
AD-A080 480

TECHNISCHE UNIV VIENNA (AUSTRIA) INST FUER CHEMISCHE--ETC F/6 11/6
THE INFLUENCE OF CHEMISTRY AND VARIOUS FABRICATION PARAMETERS 0--ETC(U)
NOV 79 B LUX, G JANGG, H DANNINGER DAERO-78-6-086

UNCLASSIFIED

NL

[or]
60
-08-180



END

DATE

FILMED

80

DOC

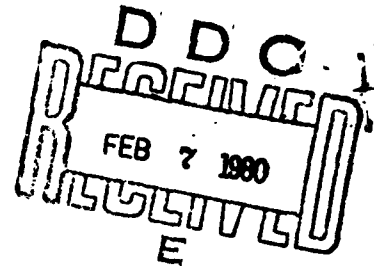
LEVEL

Grant Proposal: 2535

Grant Agreement: DAERD 78-G-086

ADA 080480

First Annual Report



The influence of chemistry and various fabri-
cation parameters on the properties of tungsten
heavy metals

DDC FILE COPY

B. Lux, G. Jangg, H. Danninger
Institut für Chemische Technologie Anorganischer
Stoffe, TU Vienna

This document has been approved
for public release and sale; its
distribution is unlimited.

80 2 6 008

DISCLAIMER NOTICE

**THIS DOCUMENT IS BEST QUALITY
PRACTICABLE. THE COPY FURNISHED
TO DDC CONTAINED A SIGNIFICANT
NUMBER OF PAGES WHICH DO NOT
REPRODUCE LEGIBLY.**

Unclassified

R&D 2535

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. REPORT TYPE AND PERIOD	
6		Final Annual Report June 78 - November 1979	
4. TITLE (and Subtitle)		5. AUTHOR(s)	
The Influence of Chemistry and various Fabrication Parameters on the Properties of Tungsten Heavy Metals.		B. Lux, G. Jangg, H. Danninger	
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)	
10 B. Lux, G. Jangg, H. Danninger		6.11.02A DAERO-78-G-086	
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
Technische Universität Institut für Chemische Technologie Anorganischer Stoffe, Vienna		IT161102BH57-04	
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE	
U.S. Army Research & Standardization Group (Europe) Box 65, FPO NY 09510		November 1979	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES	
9. Annual report (June 78 - November 79)		35	
		15. SECURITY CLASS. (of this report)	
		Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)			
Approved for Public Release Distribution Unlimited			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
(U) w alloys (U) Powder metallurgy (U) w fabrication			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
<p>The aim of this project is to improve tungsten heavy metals, particularly with regard to their ductility, porosity and density.</p> <p>The emphasis of the two-year program is to investigate the influence of the heavy metal composition (W content, binder composition) and the chemical purity of raw materials on the properties of heavy metals. In addition, particular attention is given to the influence of the fabrication conditions</p>			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified 411578

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

on the quality of the product.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	23

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

I N T R O D U C T I O N

=====

The aim of this project is to improve tungsten heavy metals, particularly with regard to their ductility, porosity and density.

The emphasis of the two-year program is to investigate the influence of the heavy metal composition (W content, binder composition) and the chemical purity of raw materials on the properties of heavy metals. In addition, particular attention is given to the influence of the fabrication conditions on the quality of the product.

A wide range of extremely varied parameter influencing the properties of W is conceivable, some are discussed in the literature (1-7), shortly summarized in the following:

a) Composition:

Increasing the W content increases primarily the density, but also the hardness, the tensile strength and the E-module. However, it reduces the ductility.

To achieve a good ductility, the binder should have a hardness and deformation properties similar to those of W grains. The most common binders are the Ni-Cu types with various ratios of alloying metals. The addition of Co to the Ni-Fe binders has proven advantageous. Binders containing Mo have also been tested. Marked improvements in the finished alloy can be achieved by adding even slight amounts of various elements.

Another important but as yet hardly investigated factor in the properties of heavy metals is the role of the binding forces between the W grains and the matrix alloy. The binding forces are linked with the wetting between the liquid binder and the W grains which is important during sintering and is also a function of interface energies.

b) Structure:

The general mechanical properties, especially the ductility, are strongly affected by the structure of the tungsten heavy metals. The optimum for good ductility is a fine grained product in which the individual grains are evenly distributed in the matrix and completely surrounded by binder with a minimum of bridging.

However through Ostwald ripening and coalescence during sintering, a pronounced coarsening of the W powder grains occurs. Thus, in general, measures which inhibit grain growth also tend to improve ductility. Little is presently known about the action of various additives which influence grain growth so that the purity of the W powder assumes a particular importance.

c) Purity of starting materials:

Since even slight amounts of additional elements in the W powder or the binder can have a considerable influence on grain growth, to obtain reproducible results it is necessary to begin with materials having the highest possible purity, or at least with those having exactly known and controllable impurities. Only in this way can the type and amount of additives be correctly selected.

d) Fabrication conditions:

Even though the sintering conditions (temperature and duration), above all because of their influence on the sintered density and on the W grain sizes, play the major role in determining the products' properties, further parameters are also of great importance.

A thoroughly mixed sinter charge from a fine grained starting material is essential for a product with desirable properties.

The compaction pressure on the green compacts is an other important factor: green compacts with a maximum density and a minimum of pressing faults are necessary to obtain a minimum residual porosity in the final products.

The compactibility of the sinter charges is a function of various factors. Measures to improve the compactibility of the powder mixtures, for example the use of coarser starting powders, can result in undesirable sintering behavior and thus in a product with inferior properties. It should be mentioned here that the rate of cooling the freshly sintered samples also influences the final properties.

e) Sintering atmosphere:

According to the literature, the sintering atmosphere could also influence the properties of the sintered products. Above all the influence of H_2 is stressed, although it is still unexplained. The usual practice today is to sinter in an atmosphere containing at least some H_2 .

f) Heat treatment:

It is also known that the thermal handling of the sintered heavy metals can strongly influence their properties. For certain compositions of the heavy metal samples, such a treatment can cause favorable structural changes.

The present work has, at least partially, to take into account all these areas. During the first year the investigations have been concentrated on the compactibility of a broad range of powder mixtures and on the influence of the sintering conditions on the properties of the heavy metal products.

The majority of the tests were made on samples with a uniform composition of 90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe, the composition commonly in use today. Usually a uniform standardized

W powder was used, for individual tests W powders with other grain sizes and different chemical purities were also checked.

1. Starting materials:

The W powders used in this work are supplied by an Austrian tungsten manufacturer. Powders with varying grain size and with different chemical purities have been made available to us (see table 1).

T A B L E 1

Mean grain sizes and chemical compositions of the W powders.

Powder	mean grain size	impurity levels in ppm									
	in μm	Al	Ca	Fe	Mo	Na	Ni	O	P	Si	C
230/78	0.74	10	7	15	492	36	17	1370	28	28	70
197/77	0.75	16	7	14	20	26	19	1180	22	40	40
234/78	0.84	16	76	18	24	20	23	1220	24	44	31
503/79	3.05	10	10	12	20	26	10	240	21	20	20
434/78	3.13	10	10	12	20	22	10	260	28	20	24
429/78	3.16	10	10	10	20	24	10	260	30	20	15
412/78	14.00	10	10	26	20	12	12	260	15	20	6

The specifications on chemical purities and mean grain sizes are given by the manufacturer. Grain sizes were determined with the Fisher subsieve sizer. These grain size distributions are in good agreement with those determined by standard sedimentation methods (original readout sheets are attached).

The powders with an average grain size near $0.8 \mu\text{m}$ have high impurity levels, especially of O_2 . The powders having mean grain sizes near 3 and $14 \mu\text{m}$ generally have the lowest impurity levels.

Our sintering tests so far have been made primarily with powders 434/78 and 503/79, both of which are available

in quantity. The two powders are from separate lots but were made using the same starting materials under the same conditions. Their chemical purities and grain size distributions are thus quite similar.

SEM photographs also show quite similar grain sizes and shapes. Grain sizes in both powders fall within a relatively narrow range. Pictures with lower magnification show that very fine powder particles are nearly absent (Fig. 1a and 1b). However as can be seen in the highly magnified shots, most of the grains are composed of agglomerates from finer particles (Fig. 2a, 2b). This is especially clear in Fig. 3b, which shows a further enlargement of the surface of the particle from 2b. For both W powders, in addition to the agglomerates (5b) single particles which are larger and denser can be observed (4a, 4b).

Powder 503/79		Powder 434/78	
Fig. 1a	1800 x	1b	2000 x
2a	1800 x	2b	3500 x
4a	9000 x	3b	10,000 x
		4b	10,000 x
		5b	10,000 x

The manufacturer will also supply us with W powders having carefully selected types and amounts of "impurity" level (doping additives). The first shipments have already arrived. These powders are to be used mainly for testing the role of impurities in grain growth during sintering and their influence on heavy metal properties.

Ni and Fe powders for the binder are supplied by the BASF company and are of carbonyl powder quality, with mean grain sizes near 15 μm . The powders were sifted in our laboratories prior to use to remove the few grains $>30 \mu\text{m}$. The elimination of the coarser fraction proved to be very important for obtaining uniform heavy metal sinter compacts. The O_2 content

of the Ni powder is 910 ppm, of the Fe 2026 ppm. Besides the usual camphor as pressing lubricant, a neutral wax (HV-wax from Hoechst) was also tested.

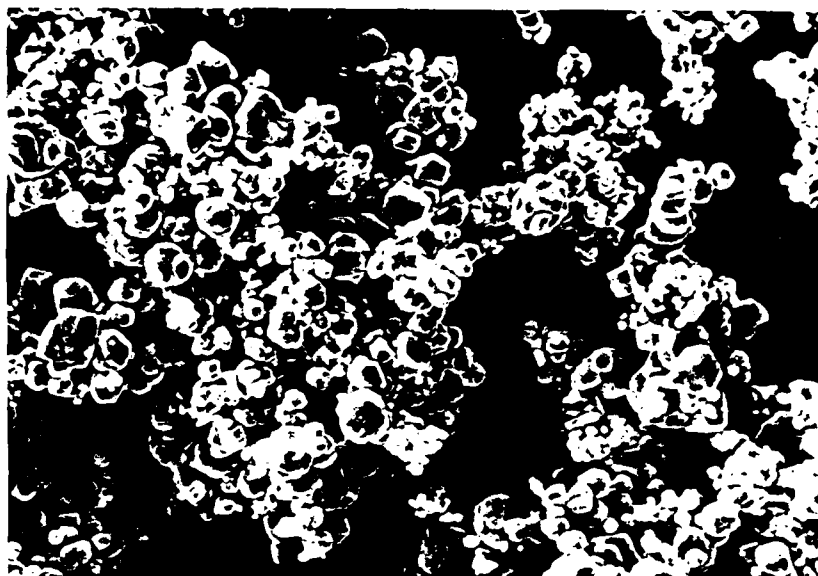


Fig.1a Powder 503/79 1800 x

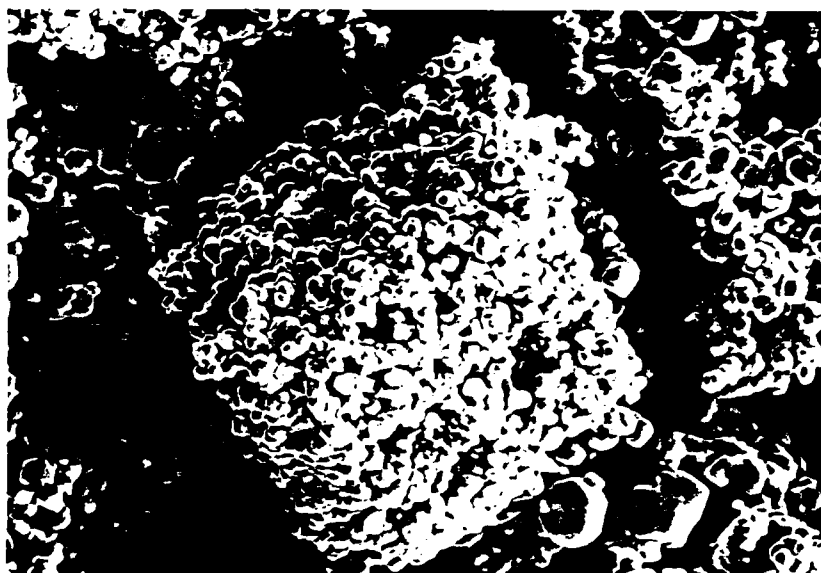


Fig.2a Powder 503/79 1800 x



Fig.4a Powder 503/79 9000 x

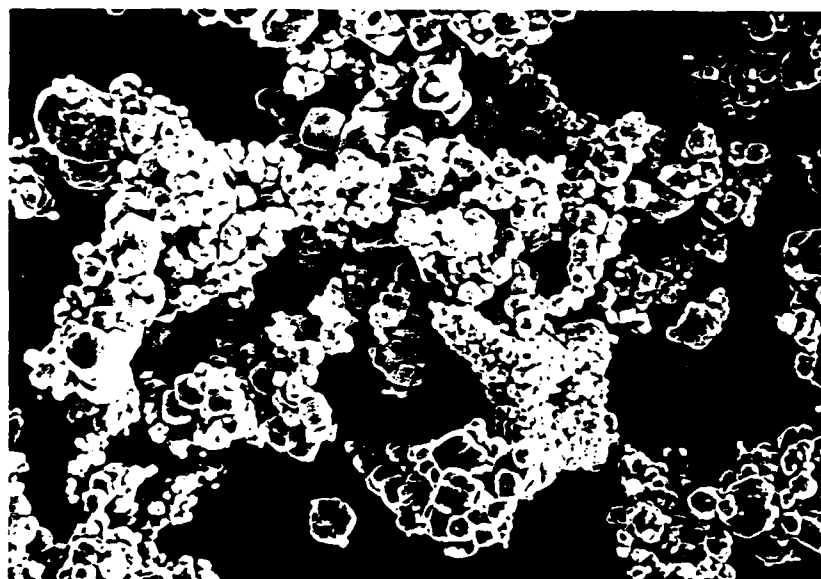


Fig.1b Powder 434/78 2000 x

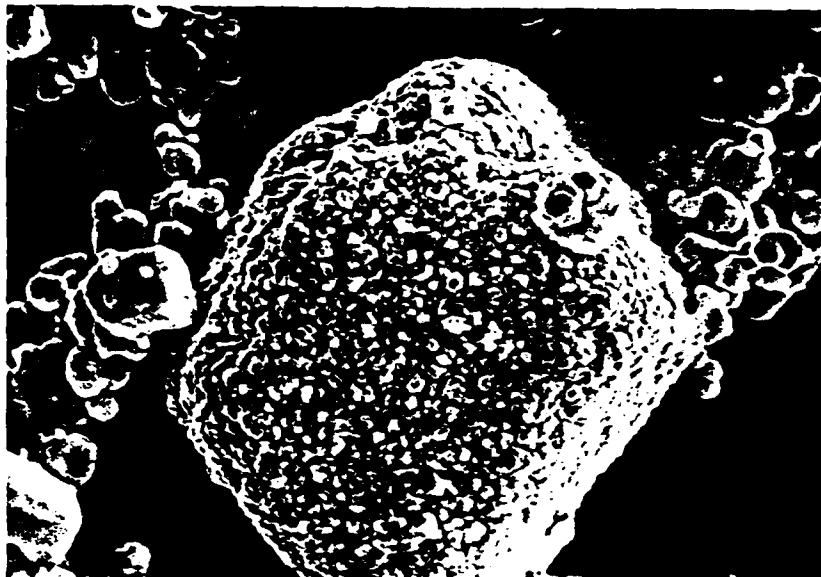


Fig.2b Powder 434/78 3500 x

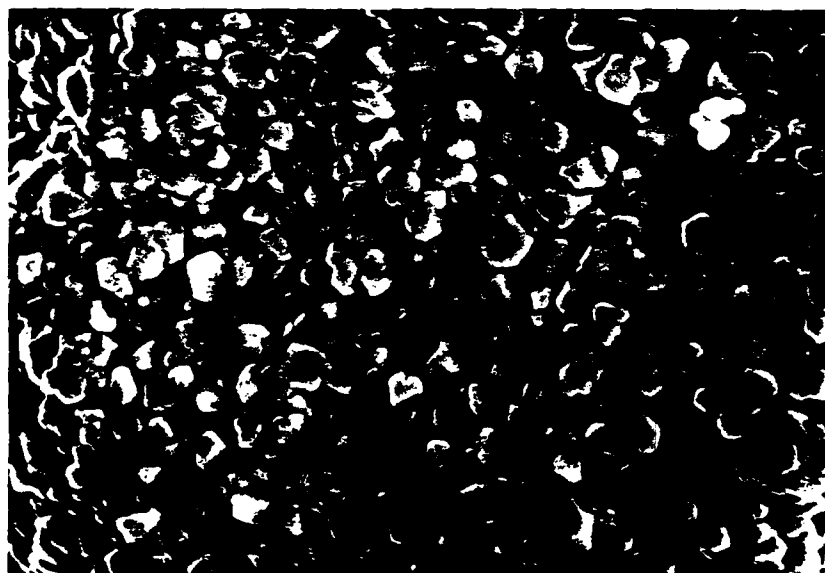


Fig.3b Powder 434/78 10000 x



Fig.4b Powder 434/78 10000 x



Fig.5b Powder 434/78 10000 x

2. Pressing behavior:

Uniform powder mixtures of 90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe were prepared using various mixing or ball milling procedures. The attainable green densities have been measured after compaction with different pressures. Various amounts of different pressing lubricants have also been tested.

2.1. Blending of the powders and granulation:

Some powder charges were wet mixed with cyclohexane for 3^{hr} in a rotation mixer, others were wet ball milled with cyclohexane for 3^{hr} in a laboratory attritor. Pressing lubricant, either 0.7 or 1 % camphor or HV-wax, was added to each sample before blending.

Following the mixing or milling process the cyclohexane was partially evaporated. The still slightly damp powder was then forced through a 0.8 mm mesh sieve for granulation and then thoroughly dried.

2.2. Bulk and tap densities of the powder charges:

The bulk and tap densities of the carefully dried powder charges were determined by standard methods. For the bulk density the powder was poured into a calibrated beaker and then weighed. For the tap density the powder was poured into a beaker being lightly shaken to help it settle and then weighed. The results are summarized in Tab.2.

T A B L E 2

Treatment and densities for the various powder charges.
Composition: 90 wt % W, 6.7 wt % Ni, 3.3 wt % Fe.

Charge	W powder	Blending treatment	Pressing lubricant	bulk density g/cm ³	tap density g/cm ³
1	230/78	mixed, granulated	1% camphor	2.45	3.63
2	197/78	"-	"-	2.37	3.45
3	234/78	"-	"-	2.80	4.09
4	234/78	attritormilled	"-	2.72	3.96
5	429/78	mixed	"-	3.72	5.28
6	429/78	mixed, granulated	"-	3.52	5.20
7	429/78	"-	0.7% HV-wax	4.22	5.83
8	429/78	"-	1 % HV-wax	4.17	5.74
9	429/78	attritormilled	1% camphor	3.71	5.42
10	412/78	mixed	"-	4.36	5.70
11	412/78	mixed, granulated	"-	4.71	5.63
12	412/78	"-	0.7% "-	4.80	5.91
13	412/78	"-	1 % EV-wax	5.15	6.07
14	434/78	"-	1% camphor	3.50	5.18
15	434/78	attritor, granulated	"-	3.58	5.21
16	434/78 ⁺	mixed, granulated	"-	3.72	5.45
17	503/79	"-	"-	3.52	5.20

⁺Fraction <1 μ m sifted off and removed.

The bulk and tap densities are primarily a function of the grain size of the starting W powder. Finer powders result in decidedly lower bulk and tap densities. The mixing or ball milling methods have only a minor influence. Attritormilled products have slightly higher densities. Granulating the charges lowers the bulk and tap densities somewhat. A further influence is exerted by the type and amount of pressing lubricant. Distinctly lower powder densities are observed

for charges with camphor than for those with HV-wax. Charges with greater amounts of pressing lubricant and medium W powder grain sizes have lower bulk and tap densities, while those with coarser W powders have higher densities.

2.3. Compactibility:

For the compactibility tests a 150 ton capacity hydraulic press with a pressing die for standard tensile strength bars was used. The pressing die (see Fig.6,7) is of a quality corresponding to that normally found in the Pm industry. The die as well as the upper and lower punches are exactly guided in the pressing frame. Thus a uniform filling of the powder sample and nearly frictionless pressing are possible. The powder is pressed simultaneously from above and from below so that the neutral - that is, the section where the powder particles do not move relative to the die wall - lies exactly in the middle of the pressed sample, a bar 5-6 mm thick.

The green densities for the various pressed samples were determined by the Hg displacement method developed in our institute. The method gives reproducible results and, as opposed to the usual determination in water, requires no pretreatment to seal the pores since Hg neither wets the green compacts nor does it penetrate into the pores.

The results of the compactibility tests are summarized in Tab.3. Pressing faults, mainly as cracks in the green compact perpendicular to the direction of the pressure, are noted as appropriate. The charge numbers correspond to those in Tab.2.

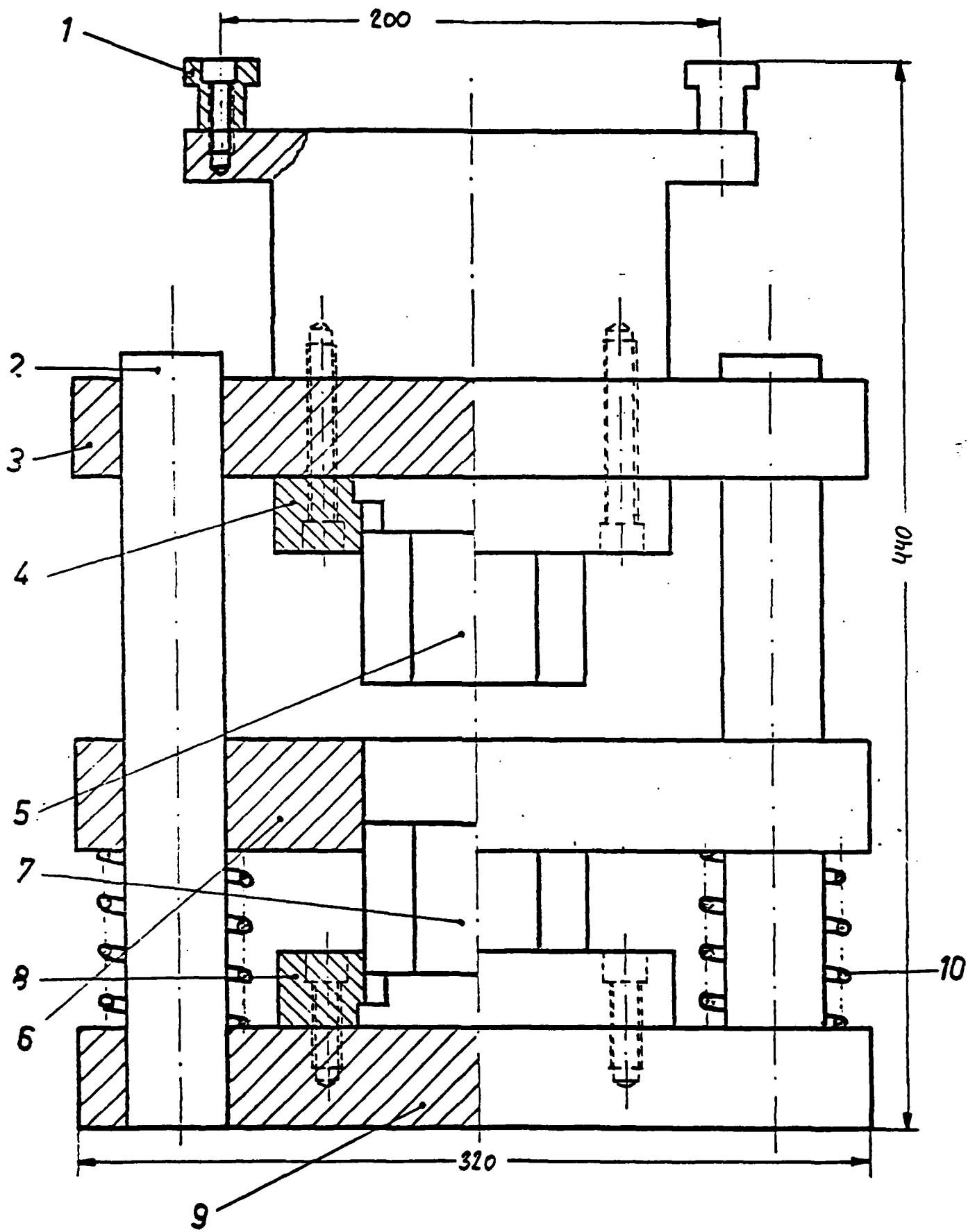


Fig.6 Pressing tool with a pressing frame for standard tensile strength bars.

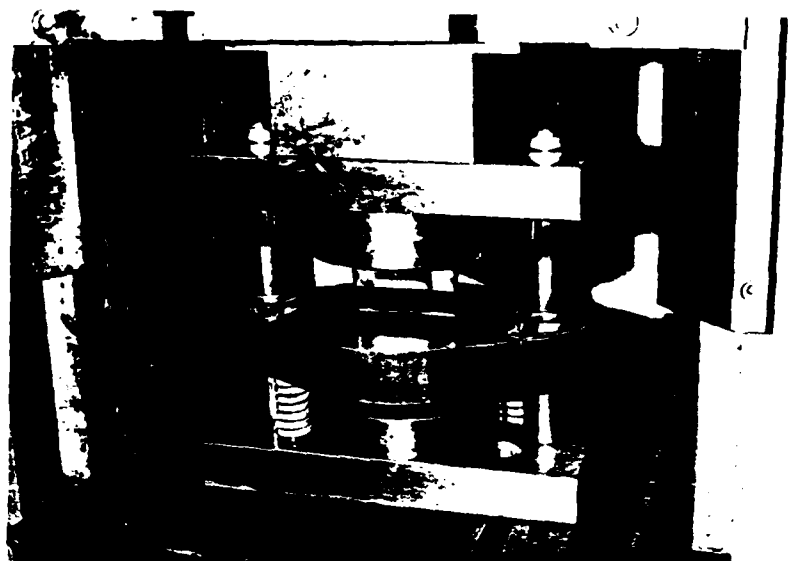


Fig.7 Pressing tool for standard tensile strength bars.

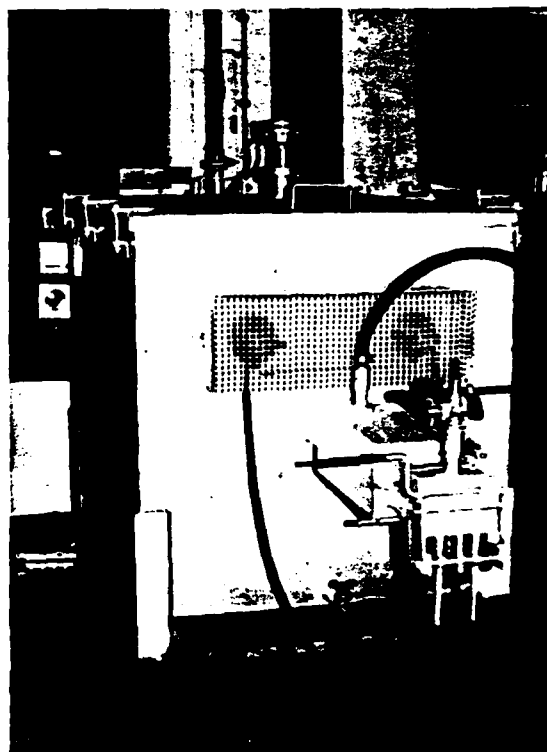


Fig.10 Sintering furnace for temperatures up to 1600°C.

T A B L E 3

Green densities for different applied pressures.

Charge	Green density (g/cm ³) at pressures (ton/cm ²) of						
	1.8	2.2	2.7	3.4	4.0	4.7	5.35
1	crumbling of the green compacts at all pressures						
2	"-						
3	"-						
4	"-						
5	9.31	9.63	10.12	10.25 ⁺	10.70	- ⁺	- ⁺
6	9.58	9.87	10.24	10.57	10.98	11.38	11.62 ⁺
7	crumbling						
8	9.43	9.86	-	10.71	- ⁺	- ⁺	- ⁺
9	9.48	9.74	10.12	-	10.78 ⁺	- ⁺	- ⁺
10	9.96	10.26	11.12	11.69	12.02	- ⁺	- ⁺
11	10.41	10.92	11.35	11.81	12.25	12.56	12.81
12	10.35	10.53	10.95	11.51	11.81	12.18	12.50 ⁺
13	10.91	11.29	11.72	12.22 ⁺	12.55 ⁺	- ⁺	- ⁺
14	9.34	9.65	10.15	10.53	10.73	11.06	11.38
15	9.34	9.65	10.15	10.53	10.73	11.06	11.38
16	9.52	9.90	10.38	10.78	11.02	11.36	11.55
17	9.30	9.66	10.14	10.48	10.75	11.10	11.38

⁺ Compression cracks perpendicular to direction of pressure

Charges with very fine W powders (1-4) could not be compacted. The resulting green compacts crumbled even as they were expelled from the die. Powders with grain sizes near 3 or 14 μ m can be pressed quite well though at higher pressures the appearance of more compression cracks were observed. The compactibility is improved and the densities are increased as W powders of larger grain sizes are used.

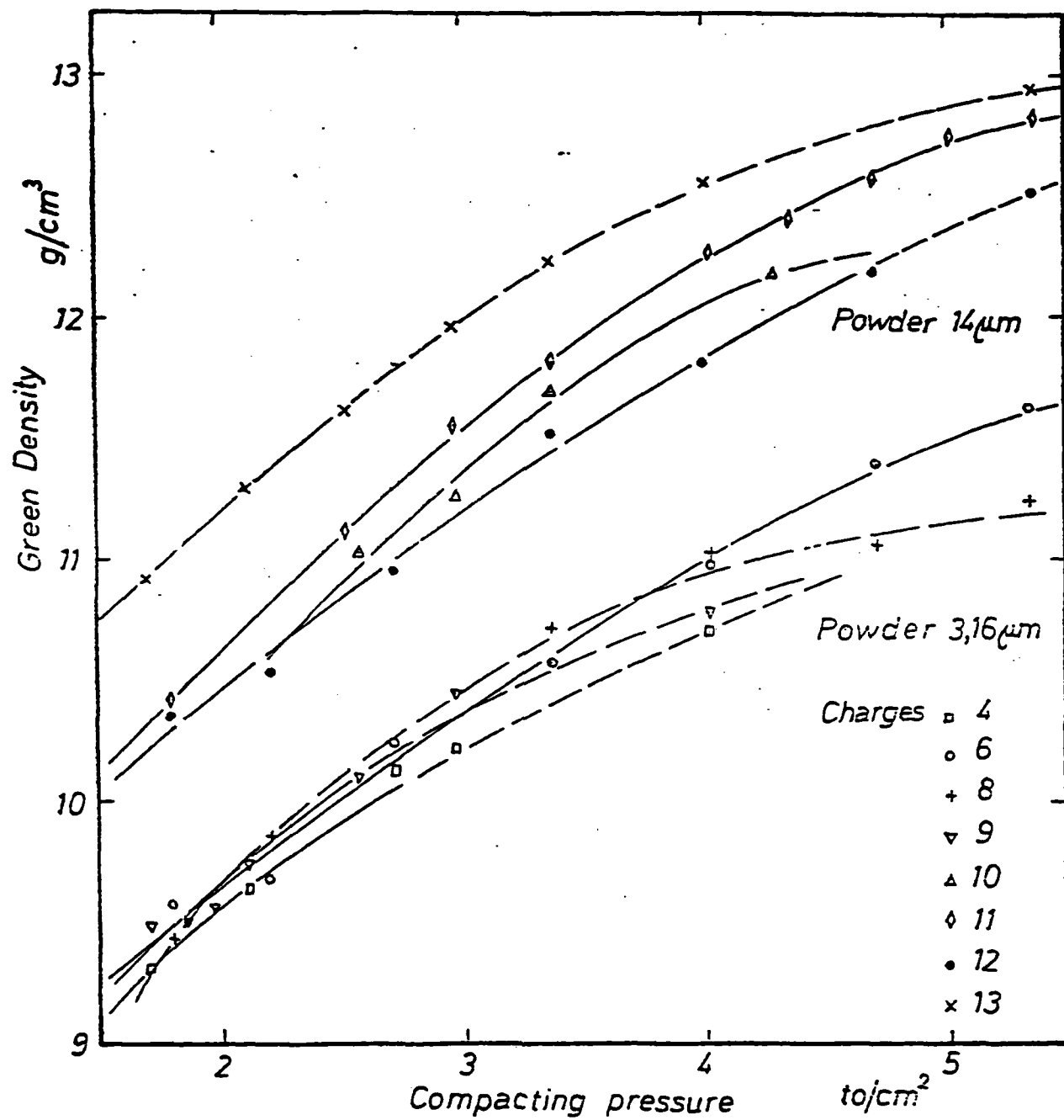


Fig.8 : Green densities of the charges 4 - 13 as a function of compaction pressure.

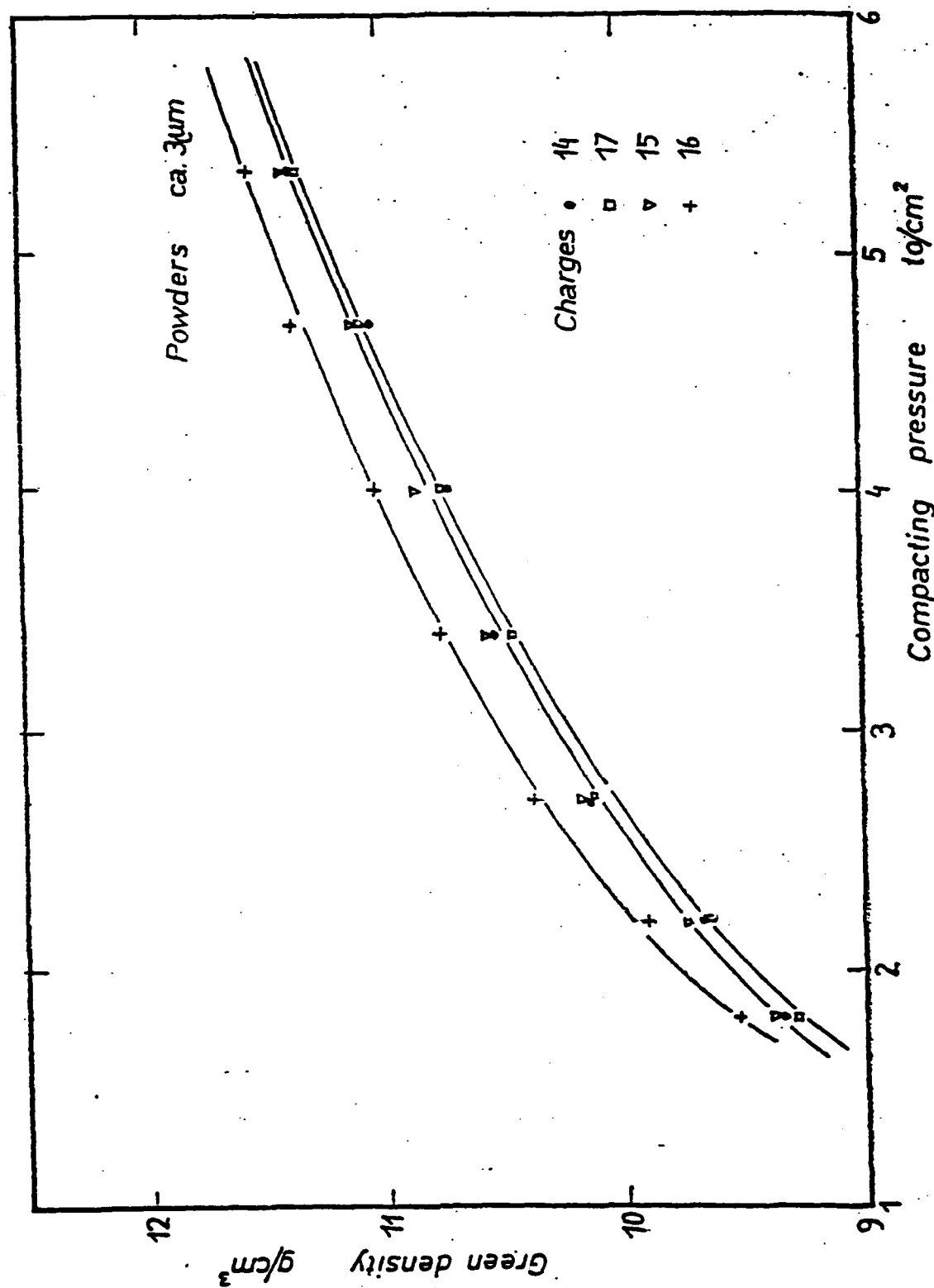


Fig.9 : Green densities of the charges 14 - 17 as a function of compaction pressure.

As can be seen from the values in Tab.3, charges with W grain sizes near $14\text{ }\mu\text{m}$ have markedly higher green densities than those near $3\text{ }\mu\text{m}$. The removal of the superfine fraction ($<1\text{ }\mu\text{m}$) by air classification from a $3\text{ }\mu\text{m}$ powder (2 % of the sample) resulted in noticeably improved compactibility- compare Fig.8 and 9. However, for industrial purposes the removal of the superfines is hardly practical because of the involved and costly procedure.

As further can be seen from Tab. 3, with Hv-wax instead of camphor as a pressing lubricant, higher green densities are obtained. However, samples with HV-wax tend to have more compression cracks. More lubricant (1 % rather than 0.7 %) appears to reduce this tendency toward cracking.

The blending treatment seems to be an important factor in obtaining higher green densities and inhibiting compression cracks. Attritormilled products are slightly less compactible. The granulation treatment proved to be advantageous when done properly: recent tests have shown that thorough drying of the granulated samples is essential for good results. Even at higher pressures no compression cracks appeared in the well dried samples, while those with even slight amounts of residual cyclohexane showed a pronounced tendency toward compression cracks. Using thoroughly dried granulated samples, the most recent tests (Charges 14-17) all produced flawless green compacts.

The dependence of the green densities on the pressure is shown in Fig. 8 and 9 (Charge numbers as in Tab. 2 & 3). Solid lines indicate flawless green compacts, broken lines the appearance of compression cracks.

2.4. Summary of the compaction tests:

The pressing behaviour of heavy metal charges is determined by a variety of factors. Above all the grain size of the

W powder is important. Fine W powders, which generally have higher O_2 contents, are unsuitable for compacting and cause severe compression cracks. The poorer compactibility of the finest powders might be linked at least partially with the greater amounts of O_2 present. A correlation exists between grain size and O_2 content. (due to oxygen pickup)

Though with increasing grain size not only the compactibility is improved, but also higher green densities are obtained, for the fabrication of heavy metals coarser W powders are not generally used as the sintered compacts should have the finest structure possible. This can best be obtained by starting with a finer W powder.

Higher pressures increase the tendency towards compression cracks, however, it appears that appropriate pretreatment of the powder charges -- intensive blending, granulation and careful drying of the granulate -- can result in sound green compacts. The higher green densities obtainable with greater pressures would be of technical interest as the denser green compacts shrink less during the liquid phase sintering, tend to distort less, and thus can be made within narrower tolerance limits. Highest pressures are however not commonly applied industrially, 3.5 ton/cm^2 generally being regarded as the upper limit. The benefits of greater green densities at higher pressures are outweighed by the accompanying decrease in tool life.

In our tests various measures were taken to improve green densities at constant pressure. The results show that natural wax is better than camphor for increasing green densities but poorer in regard to inhibiting compression cracks. Granulation causes a slight reduction in pressed densities, but very decidedly inhibits the formation of compression cracks. Attritionmilled powder charges exhibit a somewhat

poorer compactibility but the effect of the ball milling treatment is not strong.

These results are in good agreement with those reported in the literature. Although nothing seems to be reported on pressing behaviour of heavy metal charges, A. R. Poster (9) does give a detailed discussion on the pressing of pure W powders.

According to Poster, the pressing behaviour is primarily a function of the grain size and shape, with the grain size distribution being also of importance. He too notes that finer grade powders are more difficult to compact than the coarser grades. For the same compaction pressure higher green densities are obtained from coarser grades, and at the same time the tendency towards compression cracks decreases. The influence of the grain size is-as in pure W-most pronounced in the 0.8 - 4.4 μm range. With grain sizes above 8 μm the influence become much less significant. Rounded grains result in better green densities, but the green compacts have a lower strength.

3. Sintering behavior:

To determine the optimum sintering parameters standard tensile strength bars 5-6 mm thick were used. All specimens were pressed from charges with the uniform composition 90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe. The green compacts were all sintered in a H_2 atmosphere. W powders 434/78 and 503/79 with mean grain size near $3\ \mu m$ were used for the charges. The following optimal preparation procedure, as determined by the previously described test series, was used:

The starting metal powder with 1% camphor added as pressing lubricant was wet mixed with cyclohexane for 3^h in a pug mill. Most of the cyclohexane was then evaporated and the damp powder granulated, then carefully dried. All samples were compacted at $5.15\ \text{to}/\text{cm}^2$. In every case sound green compacts were obtained.

3.1. Sintering furnace and sintering process:

The sintering furnace, constructed in our laboratories, is a muffle oven (Fig. 10) with a Mo heat conducting coil which permits temperatures up to 1600°C . Because of the Mo coil the furnace must be operated in a reducing atmosphere. For all tests technical H_2 (no special purification, dew point $\sim 15^\circ\text{C}$) was used. The furnace temperature could be maintained at better than $\pm 5^\circ\text{C}$ over extended length of time.

The furnace is equipped with a shutter arrangement that allows the green compacts to be shoved into the heated furnace through the different zones. The green compacts are transported in Mo boats coated with Al_2O_3 to prevent sintering joins. By slowly pushing the samples in the appropriate zones, the sintering temperature can be reached at whatever speed might be desirable, and the compacts can be held at some particular temperature for any length of time necessary. In general the samples were held 20 min at 400°C to remove the pressing lubricant, afterwards they were

brought up to sintering temperature at different rates and were held for different length of time at different sintering temperatures. Cooling could be accomplished quickly by moving the samples directly from the hot zone to the cool zone. The slowest cooling rates were achieved by leaving the samples in the heated zone but turning the furnace off and letting them cool down as the furnace did. Fig. 11 shows schematically the time/temperature diagram (cycle 1) used for sintering the first samples.

For rapid heating the samples were shoved directly from the lubricant bake out zone into the high temperature zone, in which they reached sintering temperature within 2-3 min.

As the tests described below showed, it proved to be advantageous to leave the samples for at least 30 min in the temperature range 800 to 1000°C so they could be rapidly brought up to the sintering temperature. The sintering point is easily recognizable for the heavy metal samples: the initially light, shiny samples suddenly appear dark. Known in the literature as the "Silberblick" effect, this is due to the liquid phase that forms at the sintering temperature. It fills the pores of the green compact making the surface smooth and less radiant. The exact temperature of the bars during sintering was checked with an optical pyrometer. It agreed well with the temperature registered by the furnace regulator.

After the liquid phase appeared the samples were held for the desired length of time at sintering temperature, then cooled. During a quench cooling process, the specimens were pushed out of the heating zone into the cooling chamber as already described above. In the case of slow cooling the furnace was switched off without removal of the specimens. The temperature in the furnace first decreases relatively rapidly and after just a few minutes the eutectic melts freeze.

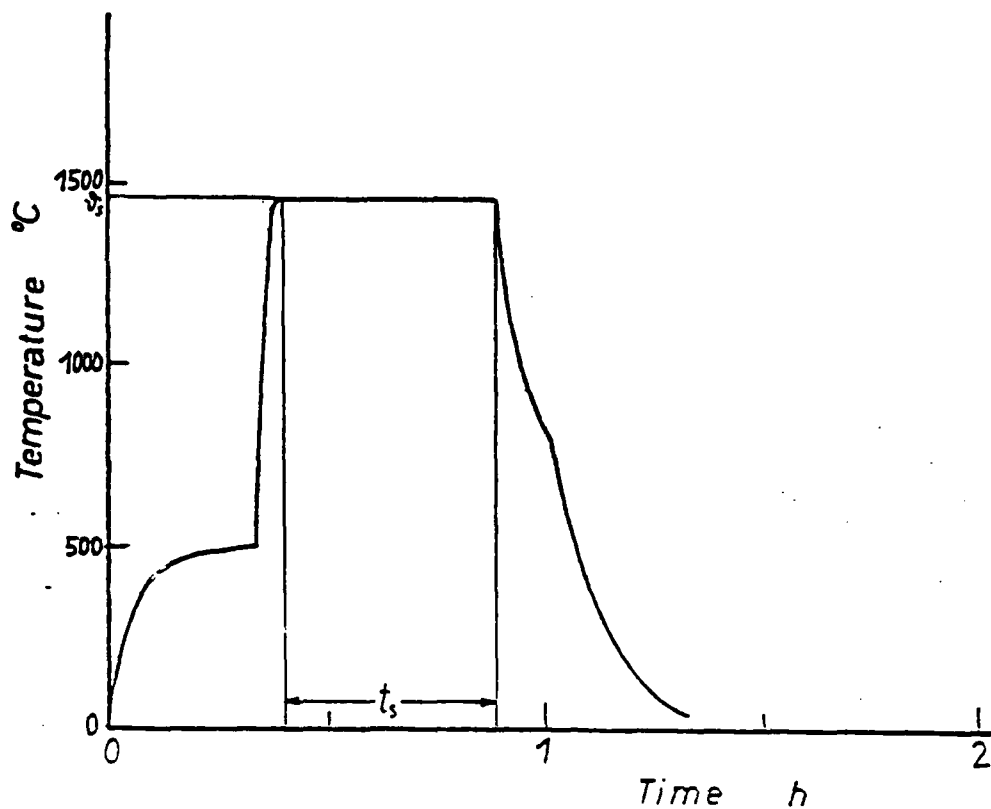


Fig.11 Temperature / time diagram for sintering cycle 1.

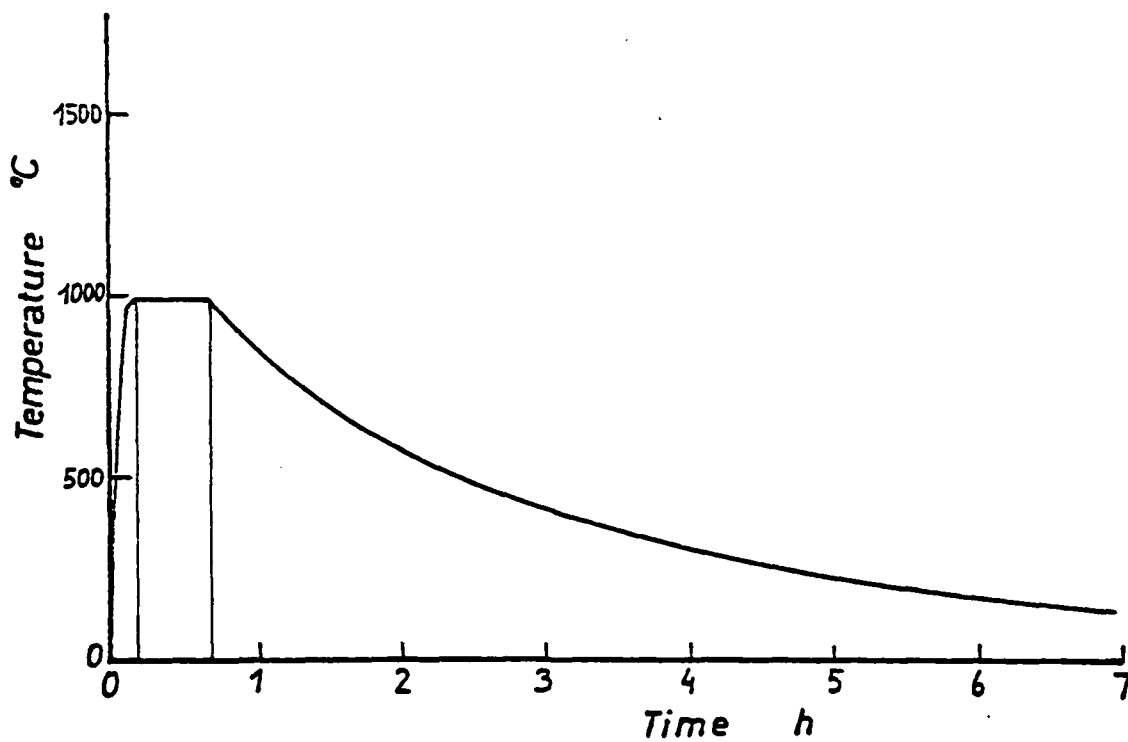


Fig.13 Temperature / time diagram for the heat treatment.

5.

About 30 min later the temperature is 1200°C. From this point on the temperature falls more slowly -- the 1200 - 800°C range, where interesting precipitates might be expected, is transversed in 4-5^{hr}. The samples which were slowly cooled were removed from the furnace only after the temperature had dropped below 400°C.

3.2. Examination of the properties of the sintered compacts:

With only a few exceptions where the sintering temperature was too high, the samples retained their original shape and were neither distorted nor deformed. However they had visibly shrunk. Initially the Hg displacement method mentioned above was used to determine the sinter compact densities. When this method was compared with the water displacement method though, it was seen that the Hg values were uniformly 0.1 g/cm³ below those measured in water. For the sintered W specimens the Hg values were also somewhat less reproducible. These differences are due to the fact that Hg does not wet the surface of the compacts, leaving residual surface pores unfilled, and in some cases small air bubbles trapped on the surface.

However, for determining the densities of green compacts which are extremely porous, the Hg method gives reliable results because there mercury's inability to wet the surface and fill the pores is an advantage.

The sinter compacts were then checked for hardness (Hv 62.5) tensile strength and ductility.

3.3. Results of the sintering tests:

3.3.1. Preliminary tests:

The first tests were made with sinter charges from different W powders but with a uniform composition of 90 wt % W, 6.7 wt % Ni and 3.3 wt % Fe. The green compacts from these charges were

compacted at different pressures, then sintered at temperatures between 1430 and 1460°C for different lengths of time. In these initial tests the samples were always heated rapidly after lubricant bake out to the full sintering temperature, and after sintering then were cooled quickly. These test results are summarized in Tab. 4. For the numbers of sinter charges used as well as the W powder type and preparation method, refer to Tab. 2.

T A B L E 4

Densities and hardnesses of different sintered W-Ni-Fe powder mixtures.

Charge	sint. temp °C	sint. time min.	compaction pressure for green ₂ compact to/cm	sint. density g/cm ³	residual porosity	hardness Hv _{62.5}
5	1460	30	1.71	16.89	1.43	292
			2.11	16.93	1.21	292
			2.71	16.92	1.23	294
			2.97	16.94	1.29	295
			4.02	16.95	1.10	299
9	1460	30	1.71	16.90	1.37	292
			1.97	16.90	1.37	295
			2.11	16.92	1.23	318
			2.56	16.93	1.19	321
			2.97	16.98	0.92	321
13	1430	30	2.11	12.84	25.1	114
			2.52	12.98	24.3	115
			2.97	13.13	23.4	124
			3.37	13.40	21.8	141
		60	1.71	13.07	23.7	124
			2.11	13.11	23.5	133
			2.52	13.25	22.6	137
			2.97	13.88	19.0	142

Charge	sint. temp °C	sint. time min.	compaction pressure for green ₂ compact to/cm ²	sint. density g/cm ³	residual porosity	hardness Hv _{62.5}
11	1440	90	3.37	14.27	16.7	182
		30	5.35	15.57	9.1	276
		30	5.35	16.98	8.8	282
		15	1.80	16.72	2.39	295
	1460		2.20	16.78	2.08	304
			2.97	16.73	2.35	303
			4.02	16.85	1.68	308
			4.70	16.88	1.57	310
			5.02	16.86	1.58	311
		30	2.20	16.92	1.30	293
			2.52	16.92	1.24	293
			2.70	16.96	1.04	298
			3.37	16.95	1.10	297
			4.02	16.96	0.99	300
			4.28	16.96	1.00	298
			5.35	16.98	0.92	302
			5.80	16.98	0.88	301
		45	1.80	16.98	0.92	290
			3.37	16.98	0.89	292
			4.02	16.99	0.85	293
			4.70	16.98	0.88	292
		60	2.52	16.98	0.91	287
			3.37	16.98	0.92	288
			4.02	16.99	0.84	289
			5.35	16.99	0.85	291
		900	3.37	17.07	0.38	271

These tests showed that temperatures of 1430 and 1440°C are insufficient. The liquid phase appears first at 1450°C. At 1460°C nearly nonporous sinter compacts are obtained. At sufficient sintering temperature the sinter compacts appear shiny and silvery, below that they are still grey. The sintering temperature of 1460°C seems to be rather too close to the

minimum necessary for liquid phase formation, later tests were thus done at 1470°C (see below).

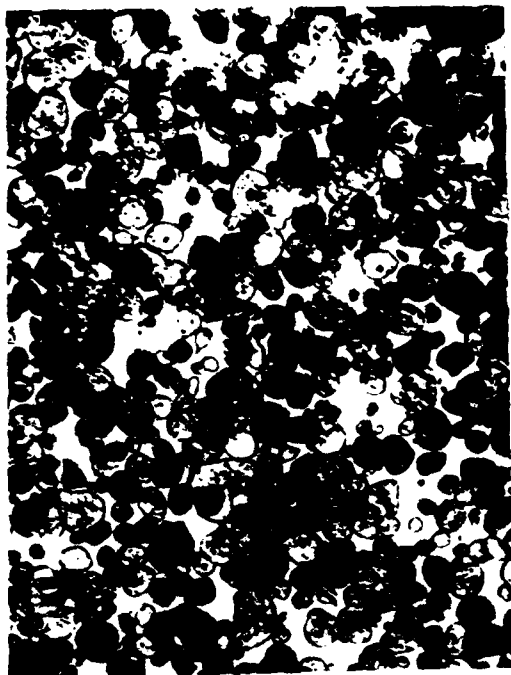
From the sintered specimens listed in Tab. 4 no useful tensile data could be obtained. The compacts were so brittle that some of them broke even before they could be fully mounted between the claps of the tensile tester. Even when it was possible to mount a compact in one piece, no measurable elongation (values < 0.1 %) and thus no meaningful ultimate tensile strength values could be obtained.

Photographs of microsections (Fig. 12a-12d) from various sintered samples in these series show that at 1460°C nearly nonporous sinter compacts are obtained. In the micrographs the grain coarsening of the W compacts during longer sintering is clearly visible. In the sinter charges from the 14 µm powder the grains are obviously larger after 60 min sintering time than after only 30 min. The microphotograph of the charge sintered for 900 min shows very coarse W grains. The charges containing W powders with mean grain sizes of 3.14 µm show a pronounced grain growth. Here the W grains have, after only 30 min sintering time, reached an average size > 10 µm.

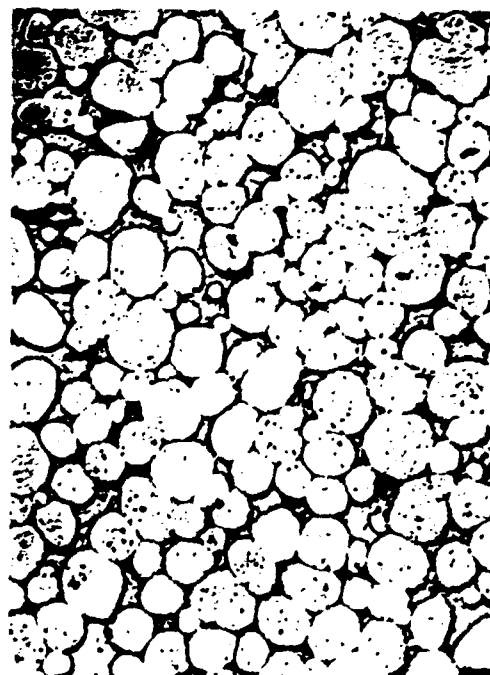
As described above only sinter compacts with very unsatisfactory properties could be obtained in these preliminary runs. The ductility was particularly poor. To find the causes of these dissatisfying results, further investigations into the influences of various parameters on the properties of the sinter compacts were necessary.

3.3.2. Influence of a postsintering heat treatment:

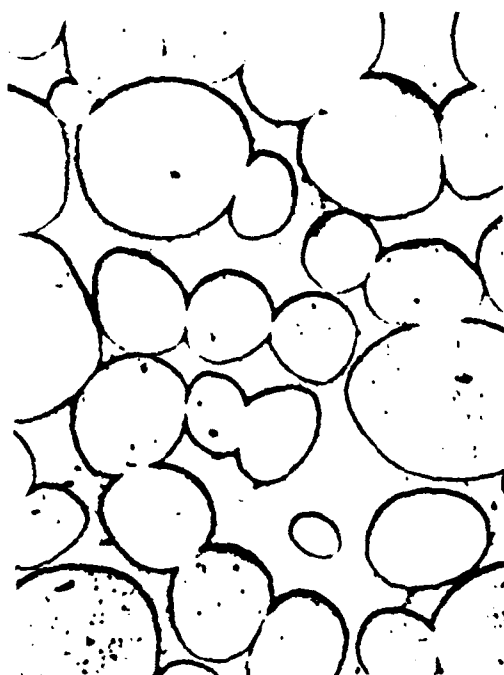
Charges from W powder 434/78 (mean grain size 3.13 µm) with 1 % camphor pressing lubricant were mixed in the pug mill or attritor milled, then uniformly granulated and pressed with 5.15 ton/cm². All samples were held at 400°C for 20 min to remove the pressing lubricant, then rapidly brought to the sintering temperature of 1470°C where they were held



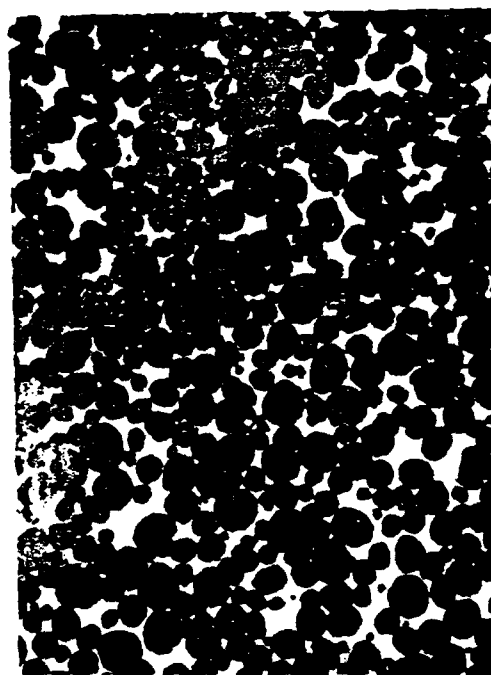
a : 14 μm , 15 min.



b : 14 μm , 60 min.



c : 14 μm , 900 min.



d : 3,16 μm , 30 min.

Fig. 12 a - d Metallographic sections of samples sintered at 1460°C for different length of time. Sintering durations and average \bar{W} grain sizes (14 or 3,16 μm) are noted.

Magnification : 250 x

for different length of time and then cooled.

For one charge the superfines ($<1\ \mu\text{m}$) were sifted off prior to mixing and granulating. The superfine fraction accounted for only a few percent of the total, but we hoped thereby to obtain sinter compacts with better properties.

The finished sinter compacts were reheated to 1000°C , held there for 30 min, then slowly cooled in the furnace (see Fig. 13).

The mechanical properties of these sinter compacts were measured and are summarized in Tab. 5.

T A B L E 5
- - - - -

Mechanical properties of the heat treated sinter compacts (rapid heating and cooling prior to and following sintering at 1470°C)

Heat treatment: reheating to 1000°C , holding for 30 min, then cooling slowly.

sint. temp. $^{\circ}\text{C}$	sint. time min	HV _{62.5}	density g/cm^3	tensile strength N/mm^2	elongation % gauge length 25mm
Sinter charge--mixed and granulated					
1470	15	299	17.10	705	0.4
	30	305	17.06	700	0.7
	60	297	17.06	674	1.1
	120	292	17.06	668	0.8
Sinter charge--superfines sifted off, powder blended and granulated					
1470	15	292	17.07	736	2.0
	30	296	17.07	742	2.5
	60	298	17.05	711	1.3
	120	294	17.03	668	1.5

sint. temp. °C	sint. time min	HV _{62.5}	density g/cm ³	tensile strength N/mm ²	elongation % gauge length 25 mm
Sinter charge--attritor milled and granulated					
1470	15	297	17.06	633	0.7
	30	293	17.06	646	0.7
	60	293	17.03	624	0.8
	120	289	17.03	642	0.7

As can be seen from these results the subsequent heat treatment brought no definite improvement in the ductility. Tests in which randomly chosen specimens were reheated to 1200-1300°C, or only to 800-1000°C, and then slowly cooled (6-8^{hr} until the temperature falls below 400°C) gave no better results. Thus, the brittleness of the sinter compacts is apparently not due to an unfavourable cooling rate.

Further, tests showed that sifting off the superfines from the W powders brought no measurable improvement. Similarly the pretreatment--mixing or milling--had no appreciable effect on the hardness or the sintered density. It is noteworthy that the sintered density in all three cases decreased slightly with extended sintering time. Attritormilled sinter charges result in sinter compacts with measurably lower tensile strength. The ductility was in all cases poor, only those charges where the superfines were sifted off showed better ductilities.

3.3.3. Influence of the lubricant removal conditions:

The possibility that the brittleness of the compacts might be due to residual C was considered. If the temperatures were increased too rapidly for the pressing lubricant to be fired out, traces of C could remain. To check this, green compacts from 90 wt % W powder 434/78 were mixed, granulated, pressed (5.15 ton/cm²) and fired out with extreme care:

over a period of 8^{hr} they were brought from room temperature to 800°C, then rapidly raised to the sintering temperature of 1470°C where they were held 30 min. Some sinter compacts were cooled quickly, some slowly in the furnace. The mechanical properties of the products from this test series are given in Tab. 6.

T A B L E 6

Mechanical properties of the sinter compacts made from green compacts with the pressing lubricant carefully removed.

Sintering temperature: 1470°C, sintering time: 30 min

	Density g/cm ³	Tensile strength N/mm ²	elongation % gauge length 25 mm
lubricant baked out slowly, cooled rapidly after sintering	17.09	493	0.2
slow bake out, cooled slowly after sintering	17.07	668	0.4
rapid bake out, cooled slowly after sintering	17.07	749	3.0

The careful removal of the lubricant from the green compacts also brought no improvement in the ductility, nor did the speed with which the compacts were cooled down from the sintering temperature appear to have a noticable effect on the ductility. Contrary to the case described in Tab. 5 where the rapidly cooled sinter compacts received a subsequent heat treatment, in the tests here the sinter compacts were not reheated but were simply cooled very slowly. This measure however brought no improvement in the properties of the final products.

C analyses of various sinter compacts, with lubricant both rapidly and slowly fired out, showed very slight C contents all in the range of 16-53 ppm (analyses courtesy of the manufacturer of the W powders). No correlation between the C contents and the ductilities of the sinter compacts could be found. Thus the possibility of too much residual C causing the low ductilities could be excluded.

3.3.4. Alloying additives in the binder:

Attempts were made to improve ductilities by adding different metals to the Ni-Fe binder. The amount of additive was always 0.2 wt % of the binder fraction, which is 0.02 wt % relative to the whole sample. Binder additives in the form of fine powders (30 μ m) from Co, Cr, Mo, V, and Cu were tested. To obtain a uniform and thorough blending of all components, all samples were wet ground for 15 min in the attritor, then granulated, dried, and pressed 5.15 ton/cm² to standard tensile strength bars. The lubricant was fired out for 20 min at 400°C, then the compacts were rapidly brought up to the sintering temperature and rapidly cooled after sintering. All sinter compacts were subsequently heat treated (30 min at 1000°C followed by slow cooling).

As can be seen from the values in Tab. 7, in certain cases improvements were realized.

T A B L E 7

Mechanical properties of green compacts with different metallic doping additives.

Each sample was attritormilled for 15 min, granulated, compacted at 5.15 ton/cm^2 , rapidly heated to sintering temperature (1470°C), sintered, cooled rapidly.

Subsequent heat treatment: reheating to 1000°C , after 30 min slowly cooling.

sint.temp. $^\circ\text{C}$	sintering time min.	density g/cm^3	tensile strength N/mm^2	elongation % gauge length 25mm
Charge with 0.02 % Co				
1470	15	17.06	754	1.5
	30	17.05	726	1.4
	60	17.06	680	1.0
	120	17.04	674	1.6
Charge with 0.02 % Cr				
1470	15	17.07	903	10.1
	30	17.05	888	11.1
	60	17.03	792	11.4
	120	17.03	814	6.1
Charge with 0.02 % Mo				
1470	15	17.06	794	1.3
	30	17.07	733	1.4
	60	17.06	743	3.3
	120	17.05	692	1.7
Charge with 0.02 % V				
1470	15	17.08	936	9.8
	30	17.06	923	10.2
	60	17.07	956	13.1
	120	17.05	892	10.0
Charge with 0.02 % Cu				
1470	15	17.01	822	1.1
	30	17.07	762	1.4
	60	17.06	704	0.8
	120	17.06	742	1.3

While additions of Co, Mo and Cu brought no appreciable improvement in the properties of the sinter compacts, additions of Cr and V gave surprisingly positive results in the ductility. Elongation values up to 10 % were obtained. The tensile strength of the compacts with Cr and V are also much better than those of others (Tab. 7). Recent tests reconfirm our experience that prolonged sintering causes a slight decrease in the density and the tensile strength. Longer sintering times are, as also noted in the literature, unsuitable for the fabrication of W heavy metals.

Tests have shown that the originally surprising effect of the Cr and V additives is due to their deoxidizing abilities-- of all the doping additives only these two bind oxygen better than the basic starting materials W, Ni and Fe.

Further tests were made to investigate the possibility that the low ductilities previously obtained were due to residual O_2 , that is, to insufficient deoxidation of the starting materials.

3.3.5. Effect of the residual oxygen:

Residual oxygen can affect the ductility of the heavy metal compacts in several different ways. It is known from the literature that oxygen levels of even several hundred ppm can cause embrittlement in Mo. A negative effect on W is known too. Residual oxygen can according to the results reported below also affect the binding forces between the W grains and the binder phase in the heavy metal.

The starting powders all have rather high oxygen contents, generally in the form of thin oxide layers on the grain surfaces. Analyses showed oxygen levels between 250 and 300 ppm. The Ni and Fe powders had much higher oxygen levels. However since the compacts are sintered under H_2 and the oxides of all three elements are easily reduced, the oxygen is usually removed.

It is conceivable that too rapidly heating the green compacts leaves the deoxidation incomplete. The first liquid phases, which are near the surface, could trap the H_2O already formed inside and prevent further H_2 from penetrating into the compact.

Therefore tests were made in which the compacts were slowly heated, particularly in the $800-1000^{\circ}C$ range where rapid reduction occurs. Here the compacts are still porous and a thorough deoxidation is possible. W powder 503/79 (mean grain size $3.05 \mu m$, O_2 level 260 ppm) was used in the usual (90 wt % W) proportion. 1 % camphor was added to the charge which was wet mixed in the pug mill, granulated, dried and compacted at 5.15 ton/cm^2 . The green compacts were placed in the cold furnace in H_2 and slowly heated. Sufficient time was thus available for baking out the pressing lubricant. The furnace required 3^{hr} to reach the sintering temperature, going from 800 to $1000^{\circ}C$ took over 2^{hr} . Thus enough time was available for reducing the Oxygen level through reaction with H_2 before sintering occurred. The temperature/time profile for these tests, "Cycle 2", is given in Fig. 14. When furnace temperature reached about $1400^{\circ}C$ the samples were temporarily held in a cooler zone until the exact temperature for sintering was reached in the furnace. Then the compacts were returned to the sintering zone for the specific length of time desired.

These sinter compacts have better ductilities (Table 8) than earlier ones similarly prepared but rapidly heated (compare Tab. 5). The rate at which these compacts were cooled also affected the ductilities: slowly cooling the compacts about doubled the ductilities.

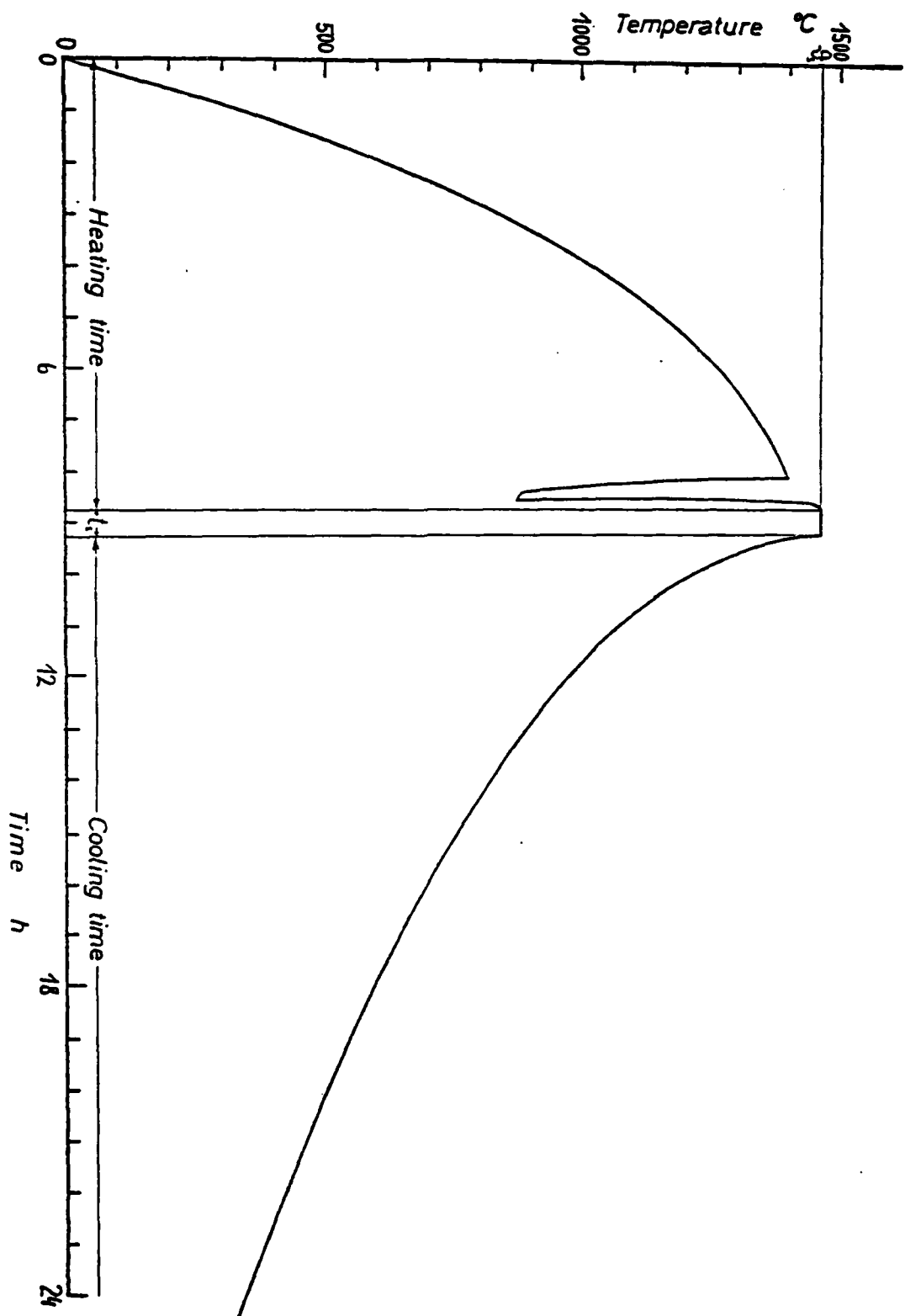


FIG. 14 Temperature / time diagram for sintering cycle 2.

T A B L E 8

Mechanical properties of samples slowly heated to sintering temperature.

(W powder 503/79, 90 wt % W, 6.7 wt % Ni, 3.3 wt % Fe, 1 % camphor, wet ground in a pug mill, granulated, compacted with 5.15 to/cm², sintered at 1470°C for 30 min)

	density g/cm ²	Hv _{62.5}	tensile strength N/mm ²	elongation % gauge length 25 mm
rapidly cooled	17.05	306	858	11.3
slowly cooled	17.06	315	998	22.4

From this same charge further green compacts were made (5.15 to/cm²) and sintered at different temperatures for different length of time to determine the optimal conditions. All samples were slowly heated to sintering temperature and slowly cooled after sintering (sintering cycle 2 in Fig. 14).

T A B L E 9

Mechanical properties of compacts sintered with different times and temperatures but slowly heated and cooled.

Preparation of green compacts as in Tab.8. Each value in Tab. 9 is the average of measurements made on 5 individual samples.

sintering temperature °C	sint. time min	density g/cm ³	Hv _{62.5}	tensile strength N/mm ²	elongation % gauge length 25 mm
1430	30	16.29	293	627	0.2
	60	16.48	298	624	0.4
	90	17.00	302	816	0.6
1460	30	17.10	306	994	24.7
	60	17.10	305	985	25.3
	90	17.09	301	924	17.2
1490	30	17.11	308	950	20.5
	60	17.07	303	988	27.7
	90	17.08	297	898	18.3

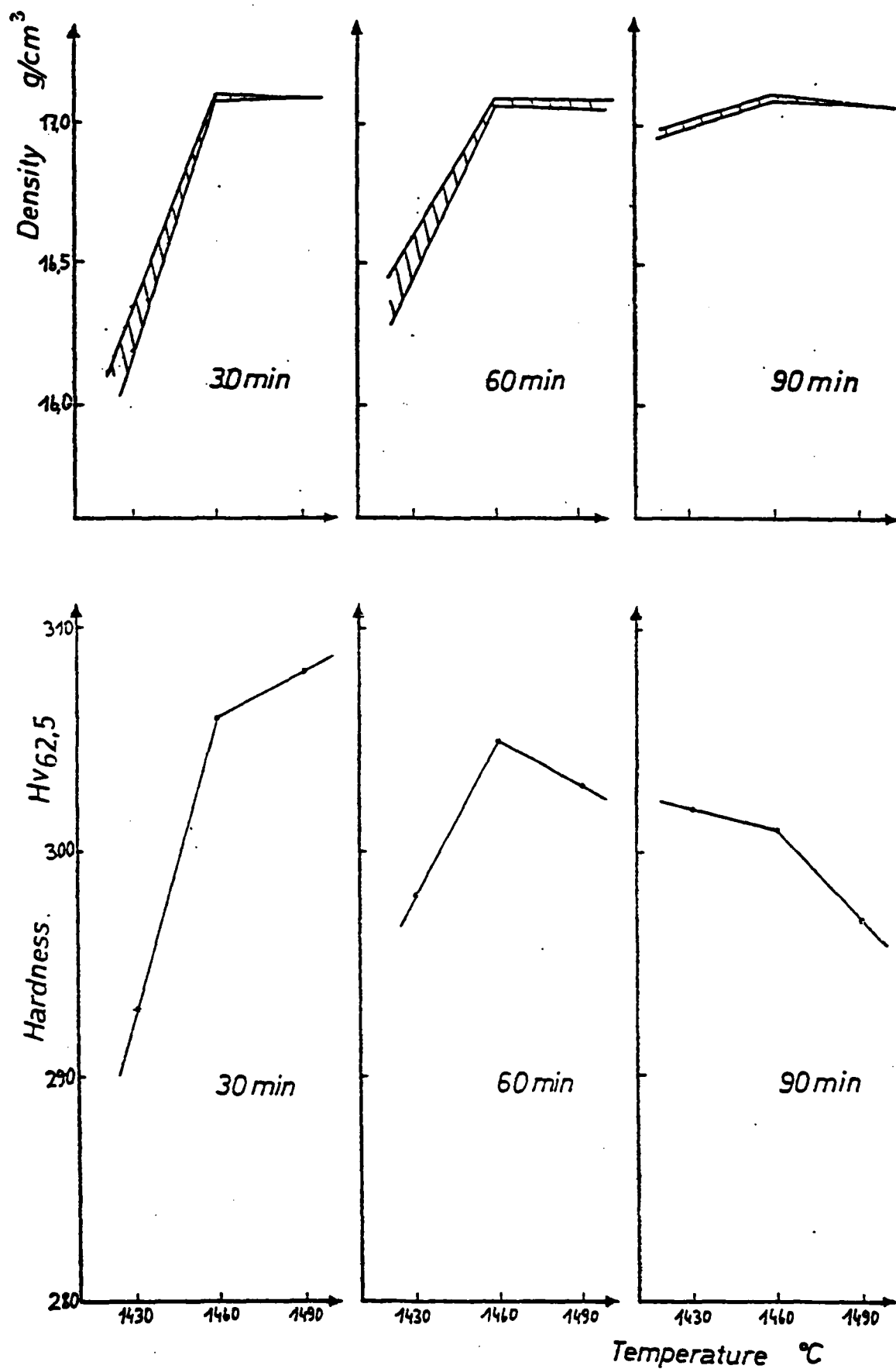


Fig.15a Density and hardness of slowly heated and cooled samples as a function of sintering temperature and time.

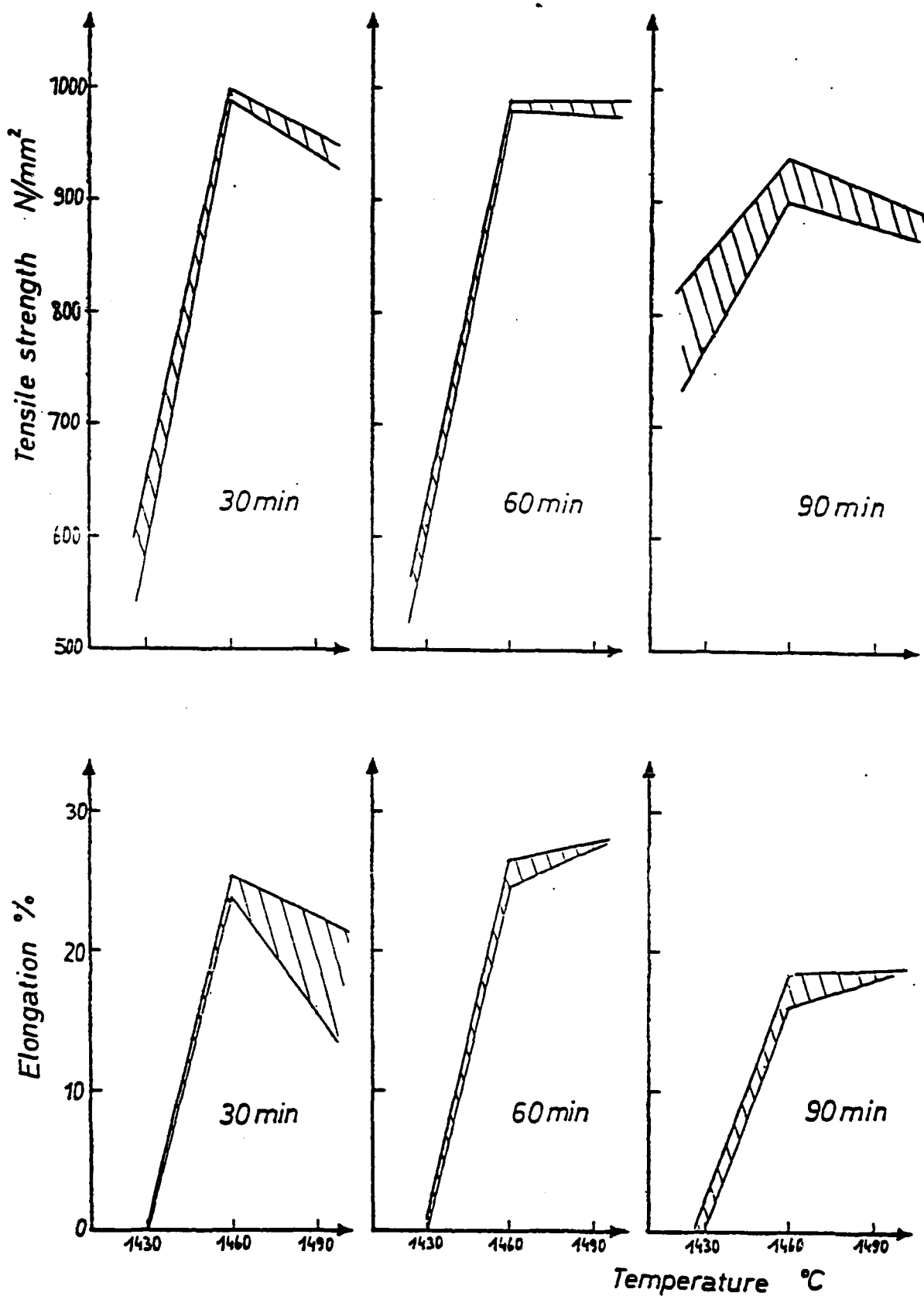


Fig.15b Tensile strength and elongation of slowly heated and cooled samples as a function of sintering temperature and time.

The individual results of the five samples tested for each of the values in Tab. 9 are shown in Fig. 15a and 15b. The narrow spread for each set of values is apparent.

The better ductilities obtained by slowly heating the samples were assumed to be due to the better deoxidation thereby possible. However, comparative Oxygen analyses, made by the manufacturer of the W powders, showed no correlation between level of residual Oxygen and ductility.

T A B L E 1 0

Oxygen levels in various sintered samples.

Charge basis	blending treatment	sintering conditions			elong. %	O ₂ ppm	
		heating	temp. °C	time min			
434/78	mixed, granulated	rapid	1470	30	rapid+HT	0.7	54
434/78	"-	rapid	1470	30	slow	0.4	57
434/78	attritormilled	rapid	1470	30	rapid+HT	11.1	85
+0.02 Cr							
503/78	mixed, granulated	slow	1470	30	rapid	11.3	53
503/78	"-	slow	1470	30	slow	22.4	85
503/79	"-	slow	1460	30	slow	24.7	51

As shown in Tab.9 1430°C is apparently insufficient for sintering, nonporous sintered samples are first obtained at 1460°C. Although their ductilities are relatively poor, the still porous specimens "sintered" below 1460°C have surprisingly high tensile strength.

As can be seen in Fig. 15a and 15b, sintering at 1460-1470°C for 30-60 min appears optimal. The final density is reached quickly at a sufficient sintering temperature and remains practically constant with increased time or temperature. Especially the hardness, and, to a lesser extend the tensile

strength, decrease as the sintering time is extended. The best ductilities are obtained by sintering for 60 min, after which they too decrease.

Increasing sintering temperatures for a constant sintering time cause decreases in hardness and tensile strength, only the ductility benefits somewhat. As can further be seen from Tab. 9, for well sintered samples a direct correlation between tensile strength and ductility appears to exist samples with higher tensile strengths also have better ductilities.

This rather unusual positive correlation between tensile strength and ductility, and their worsening with increased sintering intensity (time and temperature), had also been observed in some of our earlier work (12). This phenomenon is due to grain coarsening that progresses with the sintering intensity. The finer structures have better tensile strengths and ductilities.

3.3.5. Metallographic investigations:

Metallographic sections of differently prepared samples reveal their structural differences. While very regular structural features (Fig. 16a) are seen for the samples which were slowly heated to the sintering temperature, intermediate layers between the W grains and the binder phase can be observed for the rapidly heated samples (Fig. 16b). These layers are in the form of rings, apparently indicating a poor contact between grain and binder. Scanning electron microscope (SEM) studies confirmed this (see below). In the rapidly heated samples impurities or precipitates on the grain boundaries of the bridged grains are visible (Fig. 16c). SEM photographs (shown below) confirm the low strength of these bridges. These visible boundary lines could, as Huppmann(9) presumed, be thin layers of the binder phase which due to coalescence passed through one of the adjoining grains.

In parts of the rapidly heated but slowly cooled or subsequently heat treated samples, lamellar precipitates in the binder phase can also be observed (Fig.16d). In both the rapidly cooled and the slowly heated/slowly cooled samples no lamellar precipitates were found.

For a series of samples prepared under otherwise constant conditions (slowly heating, sintering at 1470°C, slowly cooling) but sintered for different lengths of time, the photographs clearly show the grain coarsening (Fig. 17a-17d).

The grains of the 3 μ m starting powders show clearly, even after very short sintering times (samples cooled shortly after appearance of liquid phases--"Silberblick" effect--for 2 min sintering time). uniform grains of about 15 μ m. With extended sintering the grains continue to grow but not at the same rate (Tab. 11).

T A B L E 1 1

Grain sizes (see text below) of the W grains in samples with different sintering times.

W powder	initial grain size μ m	sintering cycle	sint. temp. °C	sint. time min	final average grain size μ m
434/78	3.13	1	1470	2	14.8
				30	20.2
				60	23.6
				900	60.3
503/79	3.05	2	1460	2	14.6
				30	19.1
				60	23.2
				90	24.2
			1490	30	20.1
				60	23.4
				90	25.9

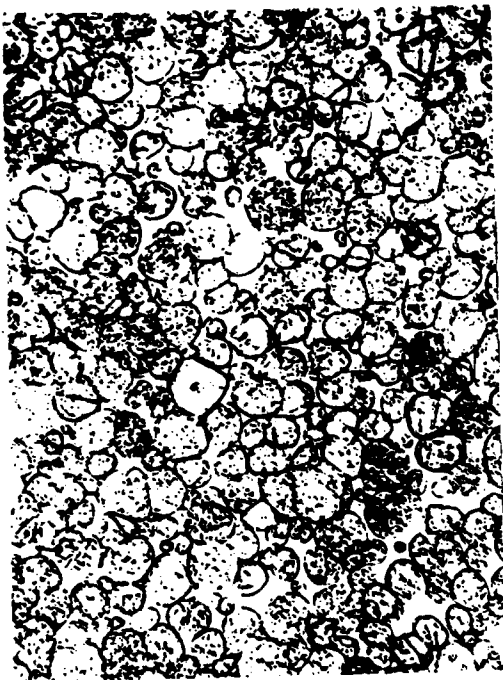


Fig.16a Metallographic section
of a slowly heated and
cooled sample. 200 x

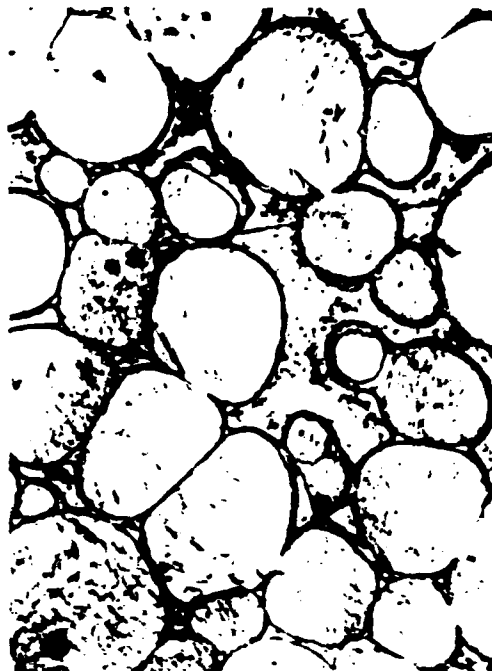


Fig.16b Metallographic section
of a rapidly heated and
cooled sample. 1000 x

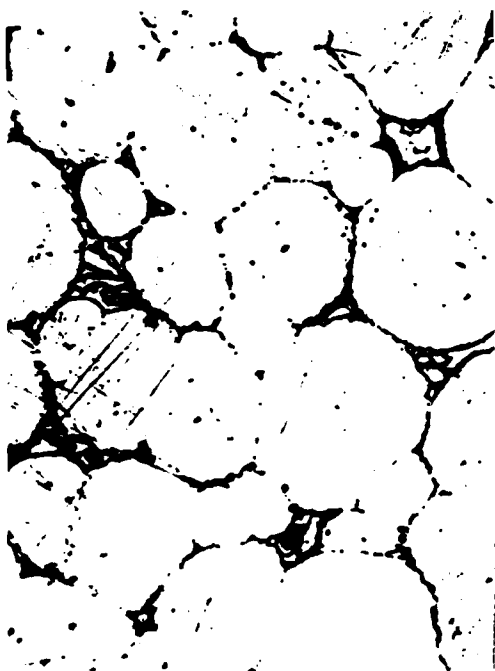


Fig.16c As Fig.16b

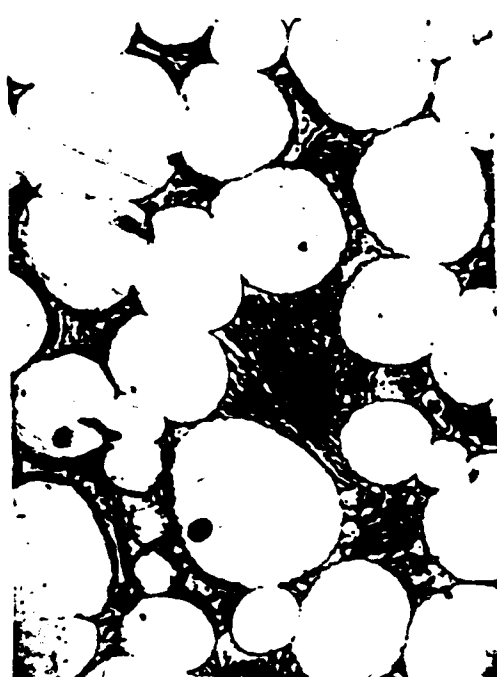


Fig.16d Metallographic section
of a rapidly heated and
cooled sample afterwards
subjected to heat treatment.
1000 x



Fig.17a 1470°C 2 min



Fig.17b 1470°C 30 min

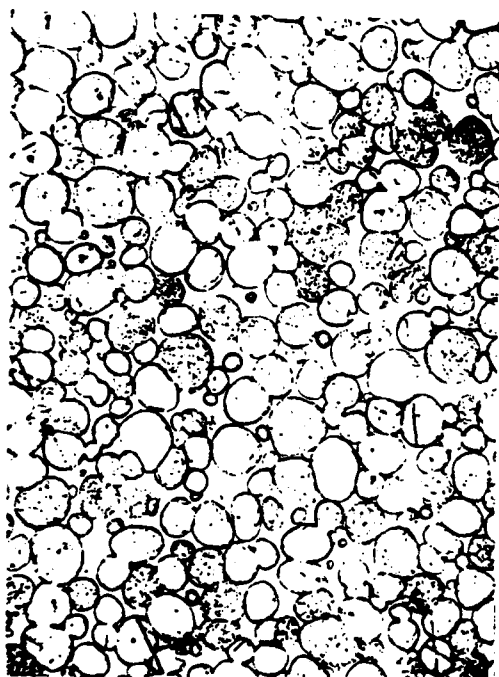


Fig.17c 1470°C 60 min

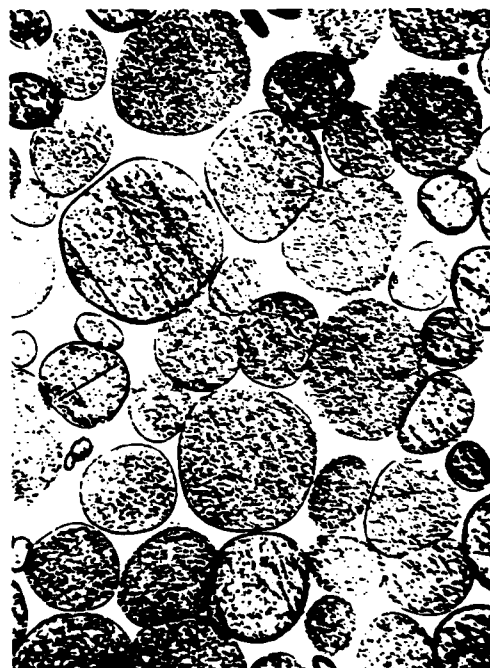


Fig.17d 1470°C 900 min

Fig.17 Metallographic sections of slowly heated and cooled samples prepared from powder 434/78 and sintered for different length of time. 200 x

The grain sizes were determined from sample sections etched with a CuSO_4 solution. For each specimen the W grains in 9 parallel 0.6 mm strips were counted and, taking into consideration the area due to binder, the average grain size was calculated. Since cut grains tend to appear smaller than they really are, the values from this method are only relative, but still quite suitable for comparisons.

The rate of heating before sintering does not seem to affect grain growth during sintering. At higher sintering temperatures a slightly faster rate of grain growth is observable. Later investigations will explore methods to slow or stop the undesirable grain growth with doping additives.

3.3.6. Effect of the cooling rate:

As already mentioned, the rate of cooling the specimens after sintering also has significant effect on the ductility. If the specimens have a high ductility, the cooling rate influences the structural development in the binder phase and thus its hardness. According to Holtz (3) good ductilities in heavy metals are achieved when the W grains and the binder have comparable hardnesses, while poor ductilities are observed for strongly dissimilar hardnesses. To test this theory the microhardnesses of the W grains and the binder phases in sintered specimens having various ductilities were measured (Tab. 12).

T A B L E 1 2

Microhardness values for W grains and binder phases from differently prepared sintered specimens.
(uniform sintering temperature of 1470°C and time of 30 min)

W Powder	sintering treatment	heat treatment	microhardness		elongation . . % gauge length 25 mm
			W grain	binder	
429/78	cycle 1	-	319	212	0.4
434/78	"-	-	312	198	0.2
434/78	"-	30min 1000°C	338	270	3.2
434/78 + 0.02 Cr	"-	30min 1000°C	335	275	13.2
503/79	cycle 2	-	310	267	25.1
503/79	"-	-	319	270	27.6

"Cycle 1" corresponds to a rapid heating and rapid cooling of the sample (see Fig. 11), "Cycle 2" to slow heating and cooling (see Fig. 14).

As can be seen from Table 12, binder hardness for samples which were slowly cooled or which underwent a heat treatment is greater, but the W grain hardness is not appreciably affected by the postsintering treatment. Thus, the slow cooling rate improved ductilities by lessening the difference between grain hardness and binder hardness.

The most important influence though seems to be the slow heating, by which, as previously discussed, through de-oxidation occurs. Otherwise similarly handled samples (rapid heating, subsequent heat treatment), but one with and one without Cr additive in the binder, showed distinctly different ductilities for essentially the same difference in hardness between W grains and binder.

3.3.7. Wettability tests:

The hardness of the W grains is not, as was first thought, a function of the deoxidation. Thus, an embrittlement of the W grains cannot be the cause of the lower ductilities found for samples which apparently still contained O_2 . The likelier cause is a lower adhesive strength between the binder and the W grains due to poor wetting of the W grains by the binder during sintering. The distinctly poorer wettability of oxygen containing W grains is known from Huppmann's investigations(8) in which rounded, very coarse W grains were used.

To find possible differences in the wettability of W grains in our powders, $5 \times 5 \times 60 \text{ mm}^3$ bars of pure W were pressed from the various powders. They were sintered for 1^{hr} at 1200°C so that they were still quite porous. These sintered bars were dipped vertically into liquid binder alloy at 1550°C . The relative height to which the liquid binder rises in the W bars should indicate the relative wettability of the W grains. However, our bars were all thoroughly saturated. It appears impossible, using our powders, to press bars sufficiently long ($>30 \text{ cm}$) to be used for this test and it had to be discontinued.

From the preliminary test it is also evident that the wettability seems to be more than sufficient in reducing H_2 atmosphere under which W heavy metals are sintered. Our tests had also included W bars sintered in a mixed H_2 - N_2 atmosphere, in NH_3 and in Ar with traces of H_2 , and all the bars had been thoroughly saturated with the liquid binder.

The SEM photographs of fracture sections from the tensile strength bars described below clearly indicate differences in adhesion in the solid state though. It should be stressed here that the relationship between the liquid phase wettability and the solid state interface bonding strength for W and the binder are not yet fully understood.

3.3.8. SEM micrographs of fracture surfaces of sintered bars:

The poor adhesion between binder and W grains is clearly recognizable in samples with low ductilities, made by rapidly heating the green compacts to the sintering temperature. Fig. 18a and 18b show that the W grains and the binder phase were literally torn apart where the bars fractured. Good adhesion can be observed in very few places. As noted above, a subsequent heat treatment for specimens so sintered brings at best only a slight improvement in ductility. In the SEM photo (Fig. 18c) of such a sample, the W grains protruding from the fracture surface are again visible, the binder did not adhere to the W grains. There are only slightly more signs of adhesion to be seen here than for the rapidly cooled samples. The ductile yield for specimens cooled slowly as well as for those subsequently heat treated is, as would therefore be expected, correspondingly only slightly higher.

Signs of a better adhesion between W grains and binder can be recognized in Fig. 18d, taken from the sintered compact doped with 0.02 % Cr. This sample also has a much better ductility.

In SEM photographs it can further be seen that W grains which had sintered together can also be torn apart (see Fig. 18d and 18e, an enlargement of such a W grain). In these photos an apparent intermediate layer between the grains is visible. The spots on the fracture surfaces indicate inclusions or impurities (Fig. 18f).

The fracture surfaces of high ductility samples heated slowly (sintering cycle 2) look entirely different. The binder adheres well to the W grains so that they are not separated when the bar breaks. Instead, the fracture goes through the W grain (see Fig. 19a and enlargement in 19b).

Thus the better ductility observed for samples sintered according to Cycle 2 (slow heating) is due to better adhesion between the W grains and binder. It is quite probable that the improved adhesion arises from a better reduction of the green compact during the slow heating before sintering.

Fig. 18 SEM photographs of the fracture surfaces of tensile strength bars sintered as in Cycle 1.

a: W powder 434/78, sintered 30 min at 1470°C, cooled slowly.
Ductility 0.4 %, 1500x.

b: As (a) but cooled rapidly from sintering temperature,
ductility 0.1 %, 3000x.

c: As (a) but rapidly cooled then heat treated, ductility
0.7 %, 1500x.

d: Charge doped with 0.02 % Cr, rapidly cooled, ductility
11.1 %, 1500x.

e: As (a), ductility 3 %, 1500x.

f: As (b), ductility 0.2 %, 4000x.

g: Excerpt from (e), 3000x.

Fig. 19 SEM photographs of the fracture surfaces of tensile strength sintered as in Cycle 2.

a: W powder 503/79, sintered 30 min at 1490°C, slowly cooled,
ductility 27.7 %, 1000x.

b: W powder 503/79, sintered 30 min at 1460°C, slowly cooled,
ductility 24.7 %, 2000x.

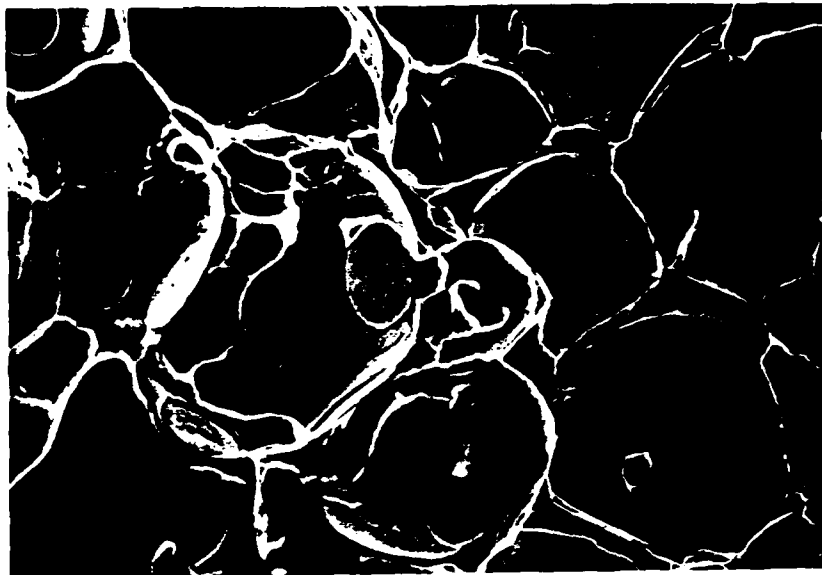


Fig.18a

1500 x

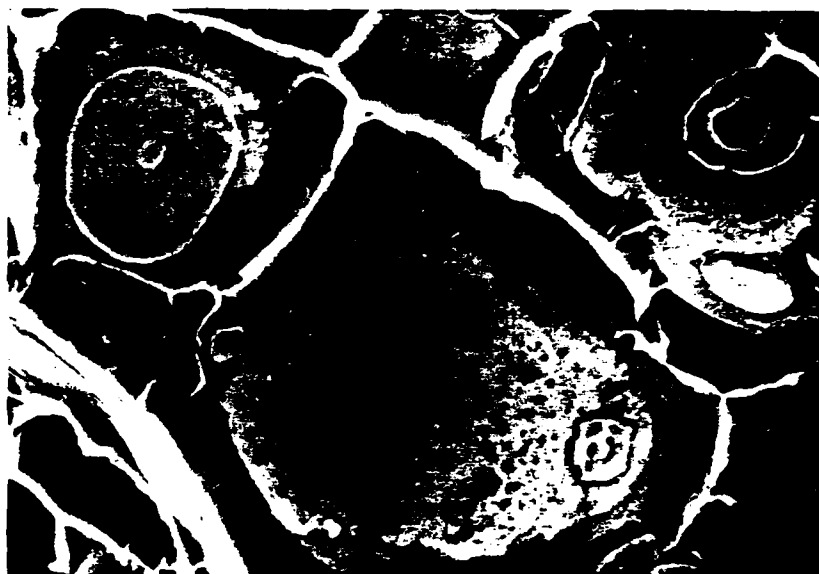


Fig.18b

3000 x

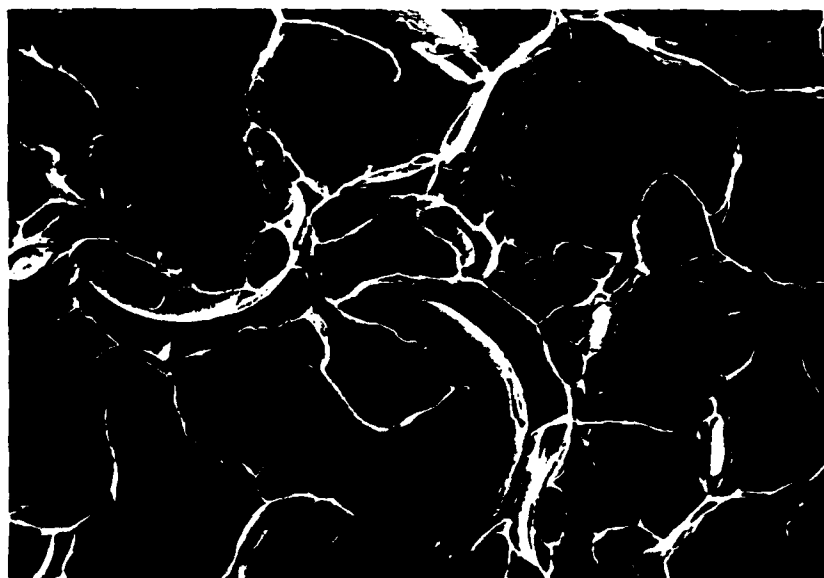


Fig.18c

1500 x

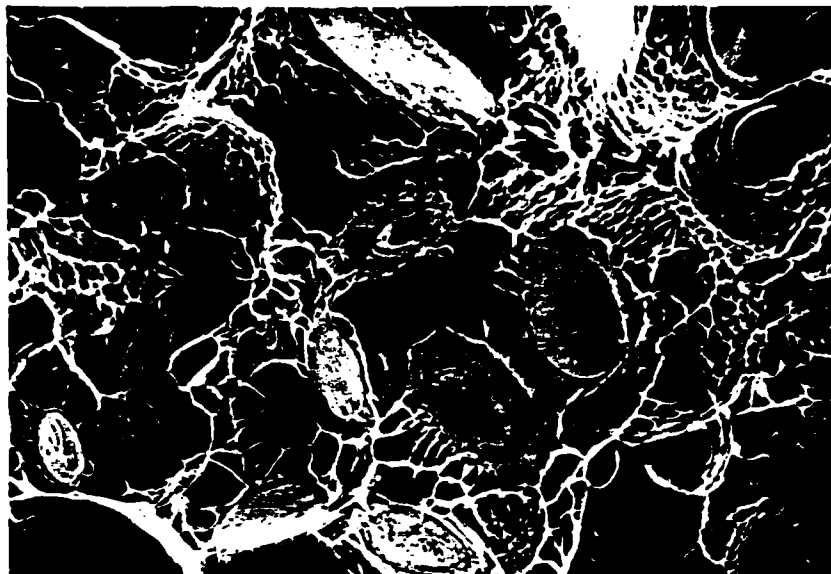


Fig.18d

1500 x

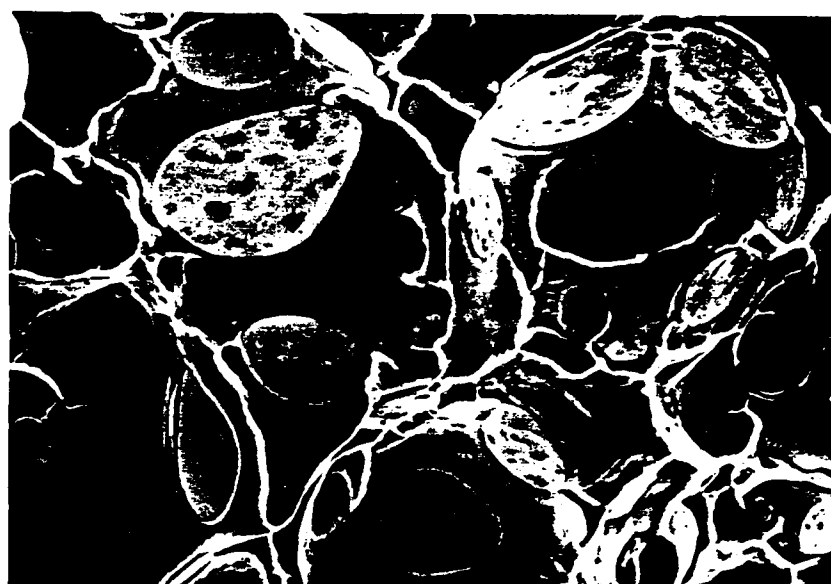


Fig.18e

1500 x



Fig.18f

4000 x

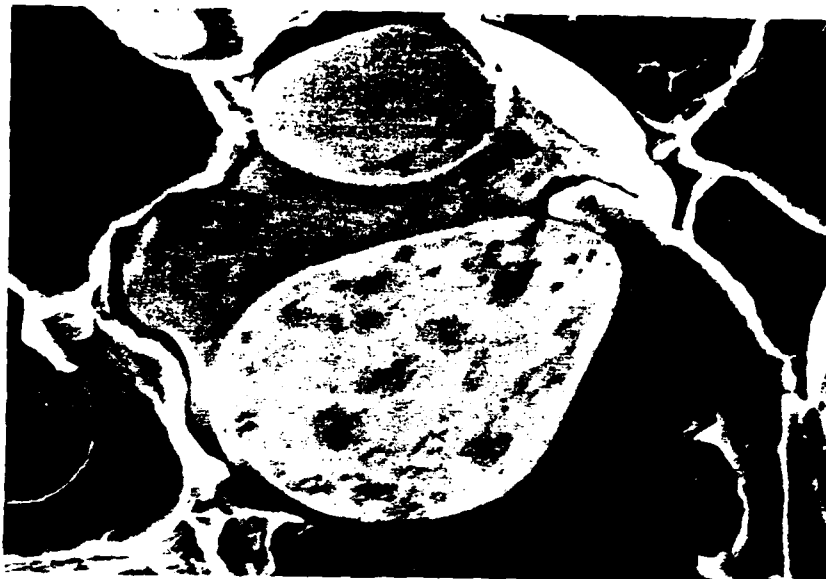


Fig. 18g

3000 x

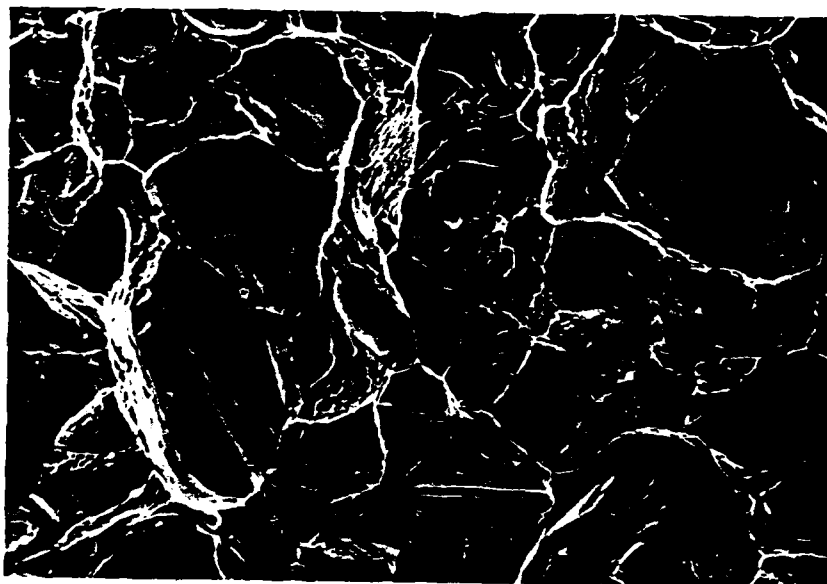


Fig. 19a

1000 x



Fig. 19b

2000 x

4. Heavy metals with higher W contents:

Especially high densities for W heavy metals can generally be achieved by increasing the W content. Alternative measures such as adding uranium (2) or other specifically heavy metals to the binder have little effect because the binder accounts for so little of the entire sample. According to Ariel, Barta and Branton (10), increasing the W content for a given binder composition increases the hardness slightly and decreases the ductility, also slightly. Tensile strength is less affected by the W content.

Our investigations included test with 95 and 97 wt % W charges to determine their optimal sintering conditions and the final mechanical properties. W powder 434/78 was used and the Ni:Fe ratio in the binder was maintained at 2:1. The preparation included the addition of 1 % camphor and ball milling with cyclohexane followed by granulation.

4.1. Compactibility of the high W charges:

The green densities obtained at different compaction pressures are given in Tab. 13 and Fig. 20.

T A B L E 1 3
- - - - -

Green densities from charges with higher W contents at different pressures.

W content	density (g/cm^3) at a compaction pressure (to/cm^2) of			
	2.6	3.4	4.3	5.15
95 wt %	11.02	11.58	11.91	11.03 ⁺
97 wt %	11.14	11.61	12.01	12.13 ⁺

⁺compression cracks

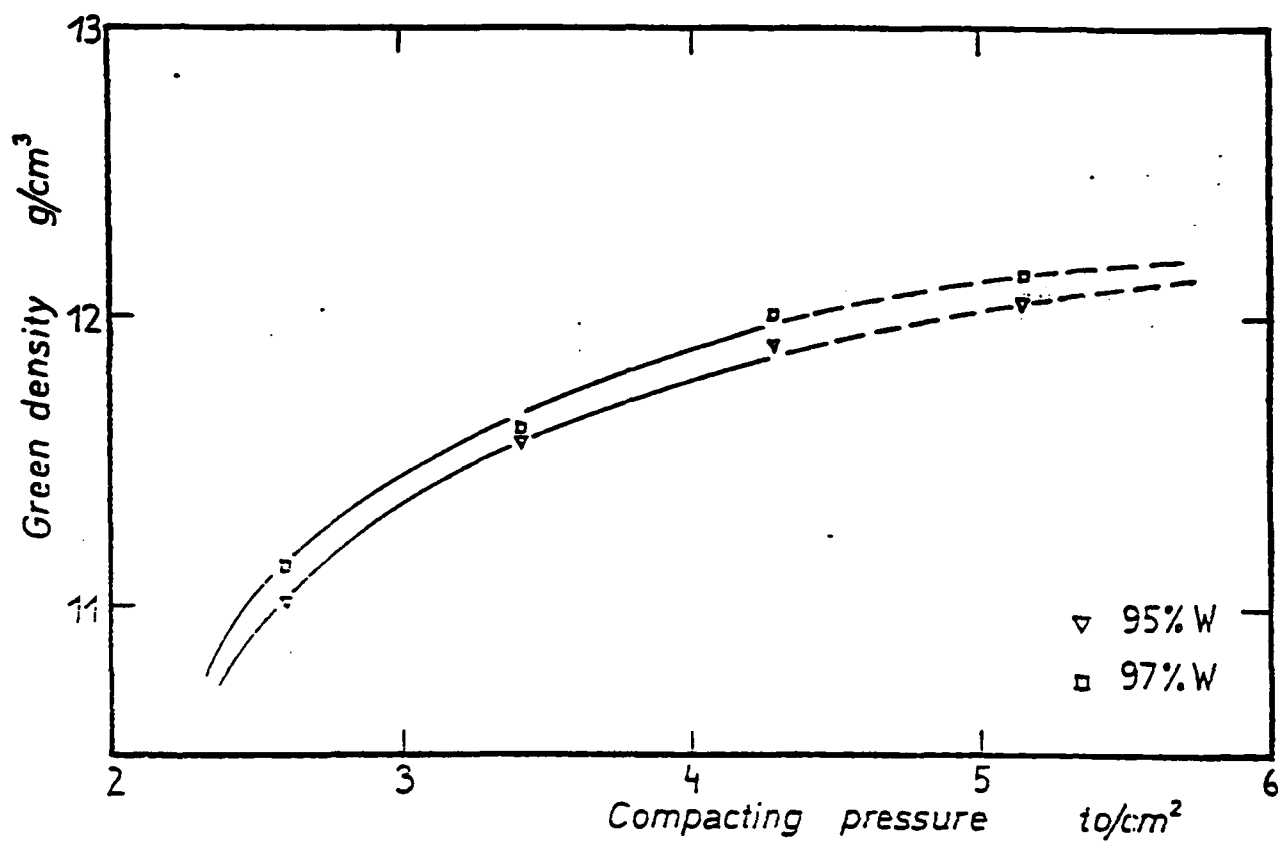


Fig.20 Green density of heavy metals with higher W - contents as a function of compacting pressure.

Distinctly higher green densities are obtained with 95 wt % W than with 90 wt % (compare Tab. 3). A further increase to 97 wt % W has no appreciable effect, apparently because the charges with so much W are so difficult to press. |

Contrary to the green compacts with 90 wt % W, some of those with 95 and 97 wt % W already had compression cracks when compacted at 5.15 to/cm^2 . As green densities are relatively independent of compaction pressure, we used 4.3 to/cm^2 in order to obtain sound green compacts .

4.2. Sintering the high W samples:

Preliminary tests showed that $1460-1470^\circ\text{C}$, although optimal for sintering charges with 10 % binder, is apparently too low for sintering the high W samples. At these temperatures the sintered compacts had 1.5-2 % residual porosity, while higher temperatures gave nonporous samples. Thus the high W samples were sintered at 1490°C .

The green compacts were heated slowly (Cycle 2) and in general cooled slowly, these conditions having been recognized by then as being best. For comparison several samples were heated slowly but cooled rapidly after sintering.

The mechanical properties of these sinter compacts are listed in Tab. 14.

T A B L E 1 4

Mechanical properties of sintered specimens with higher W contents.

Samples compacted at 4.3 to/cm^2 , heated slowly, sintered at 1490°C .

	sintering time min	cooling	density g/cm^3	HV _{62.5}	tensile strength N/mm^2	elongation % gauge length 25 mm
95 % W	15	slow	18.08	317	863	5.1
	30	slow	18.09	312	965	13.1
	30	rapid	18.08	308	906	7.2
	60	slow	18.07	312	898	8.7
	90	slow	18.12	305	851	5.0
	120	slow	18.13	302	876	6.9
97 % W	15	slow	18.46	293	873	2.0
	30	slow	18.52	316	898	4.2
	30	rapid	18.52	317	840	2.8
	60	slow	18.51	312	831	3.3
	90	slow	18.55	314	812	2.6
	120	slow	18.53	312	835	4.2

The values of the mechanical properties as a function of sintering time are shown in Fig. 21a and 21b. As can be seen, for obtaining good ductilities and high tensile strength, 30 min appears to be the best sintering time. The sintered density increases slightly with extended sintering. Very few pores remain, apparently because of the relatively small proportion of binder, and these close with prolonged sintering. However the gain in density is much less than the extensive losses in tensile strength and ductility resulting from the longer sintering. The hardness also decreases with increased sintering time, due to the increased W grain coarsening which is observed again in these samples.

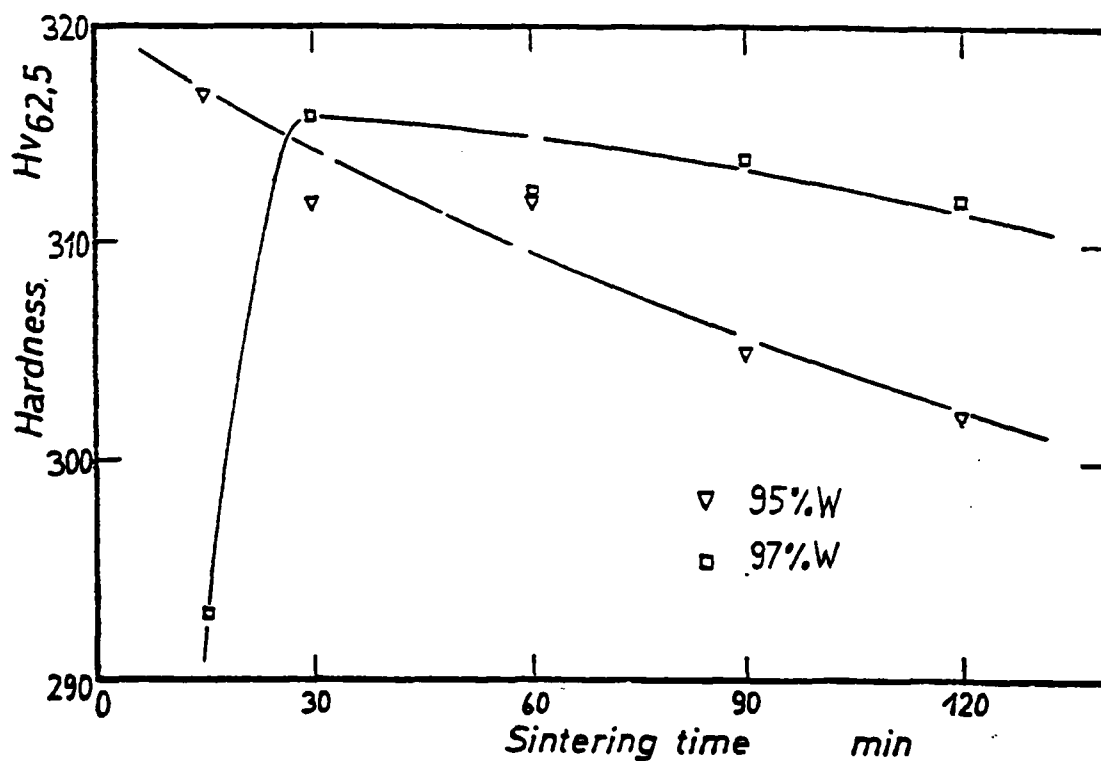
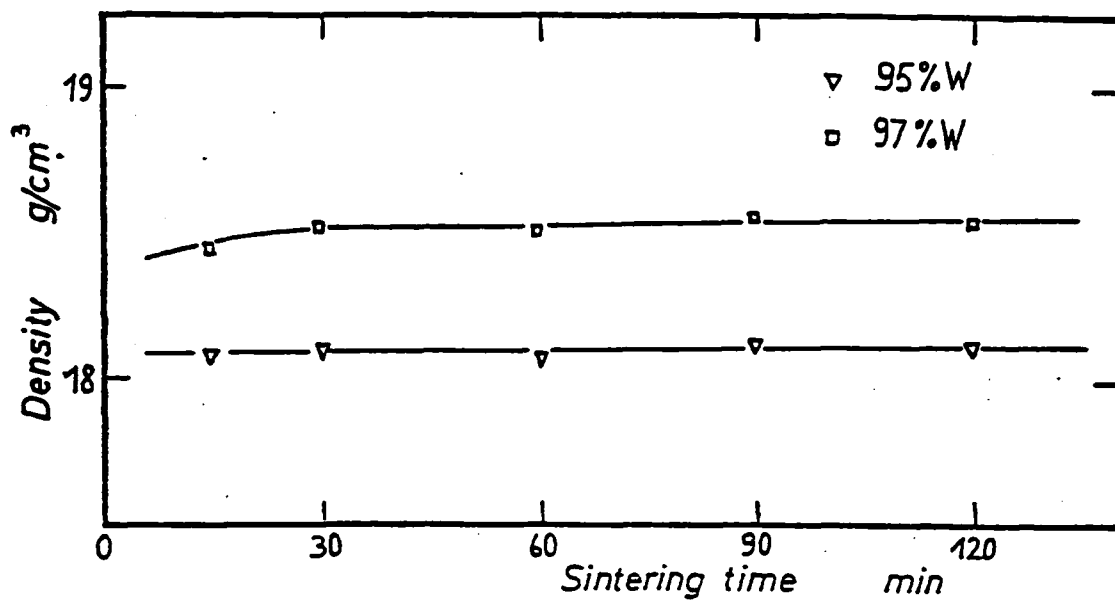


Fig.21a Heavy metals with higher W - contents sintered at 1490°C :
Density and hardness as a function of sintering time.

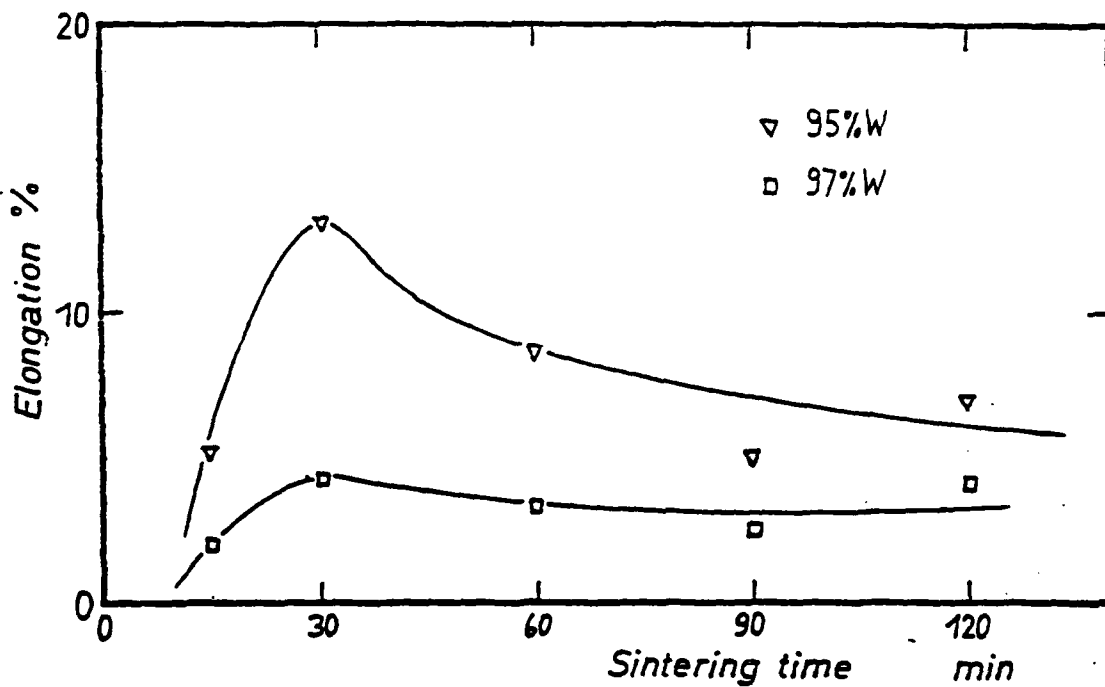
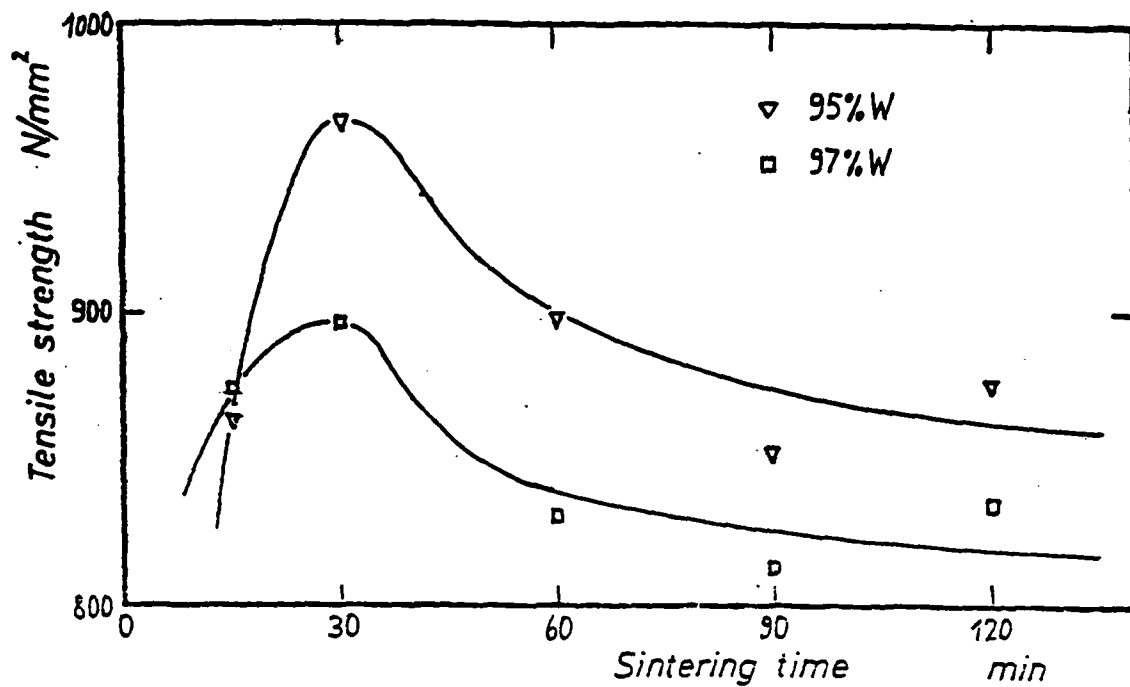


Fig.21b Tensile strength and elongation as a function of sintering time.

As a comparison between the values in Tab. 11 and Tab. 9 shows, the hardness increases with increasing W content, but not decidedly. While samples with 90 wt % W have HV = 300-305, samples with 95 wt % W have hardnesses around 310 and 97 wt % W, near 315.

As expected the tensile strength decreases with increasing W content, though not substantially. The W content has a greater influence on ductility. Samples with 90 wt % W have ductilities of 20-25 %, those with 95 % W just up to 13%, and with 97 % W only slightly over 4 %. The influence of the cooling rate is also apparent for the ductilities of the high W samples. Rapid cooling causes distinctly lower ductilities than slow cooling.

5. Summary:

The first goal of this project, to fabricate sintered heavy metals with good tensile strengths and ductilities, has been reached. With 90 wt % W and 10 % Ni-Fe binder in the ratio 2:1, sintered specimens with tensile strengths of 950-1000 N/mm², ductilities up to 27 % and densities near 17.10 g/cm³ were achieved. With 95% W densities near 18.0 g/cm³, tensile strength over 900 N/mm² and ductilities up to 13 %, with 97 % W densities over 18.5 g/cm³, tensile strengths up to 900 N/mm² and ductilities over 4 % were attained.

Extensive tests on the pressing behavior of the sinter charges showed the best compactibility and the highest green densities are attained by adding 1 % camphor to the powder mixture and wet blending it with cyclohexane. This is then evaporated till the powder is crumbly, the right consistency for granulation. The granulate must then be thoroughly dried. Alternatives, such as attritor ball milling the powder charge, using other pressing lubricants, omitting the granulation, or incompletely drying the granulate, worsen the compressibility. Powders unfavorably prepared frequently have compression cracks even at lower compaction pressures, while properly prepared powders give sound green compacts at 5.15 To/cm².

Investigations of many sintering parameters have shown that nonporous sintered specimens are possible only above 1460°C. Enough eutectic melt for liquid phase sintering cannot form below that. Higher W contents (95 and 97 wt %) require an even higher sintering temperature. Further, 30 min was found to be the optimum length of time for sintering. Longer sintering causes too much grain coarsening which lowers the final mechanical properties.

The deoxidation of the green compacts prior to sintering has a substantial effect on the quality of the product. The best deoxidation is achieved by slowly heating the green

compacts in H_2 up to the sintering temperature, with a longer holding time in the 800-1000°C region. Poor pre-reduction gives brittle sintered specimens with low ductilities. Residual C, possibly from too rapidly baking out the pressing lubricant, could not be established. Improved ductilities through doping with reducing metals (Cr, V) were realized, while doping with nonreducing metals (Co, Mo, Cu) had little influence on the ductilities. The post sintering treatment of the samples is also important, slow cooling from the sintering temperature or a subsequent heat treatment for rapidly cooled samples is necessary for favourable structural development in the binder phase. Appropriate postsintering heat treatment approximately doubles ductilities as compared to simply cooling the samples rapidly.

During the slow cooling process the binder becomes much harder. W grains and binder then have similar hardnesses which, according to the literature is desirable for high ductilities.

The decisive realization however appears to be that the complete removal of oxygen prior to sintering necessary for obtaining good quality heavy metals. Inferior batches during production could be due to poor reduction of the sintering specimens. This point will receive particular attention in future studies.

6. Further Program :

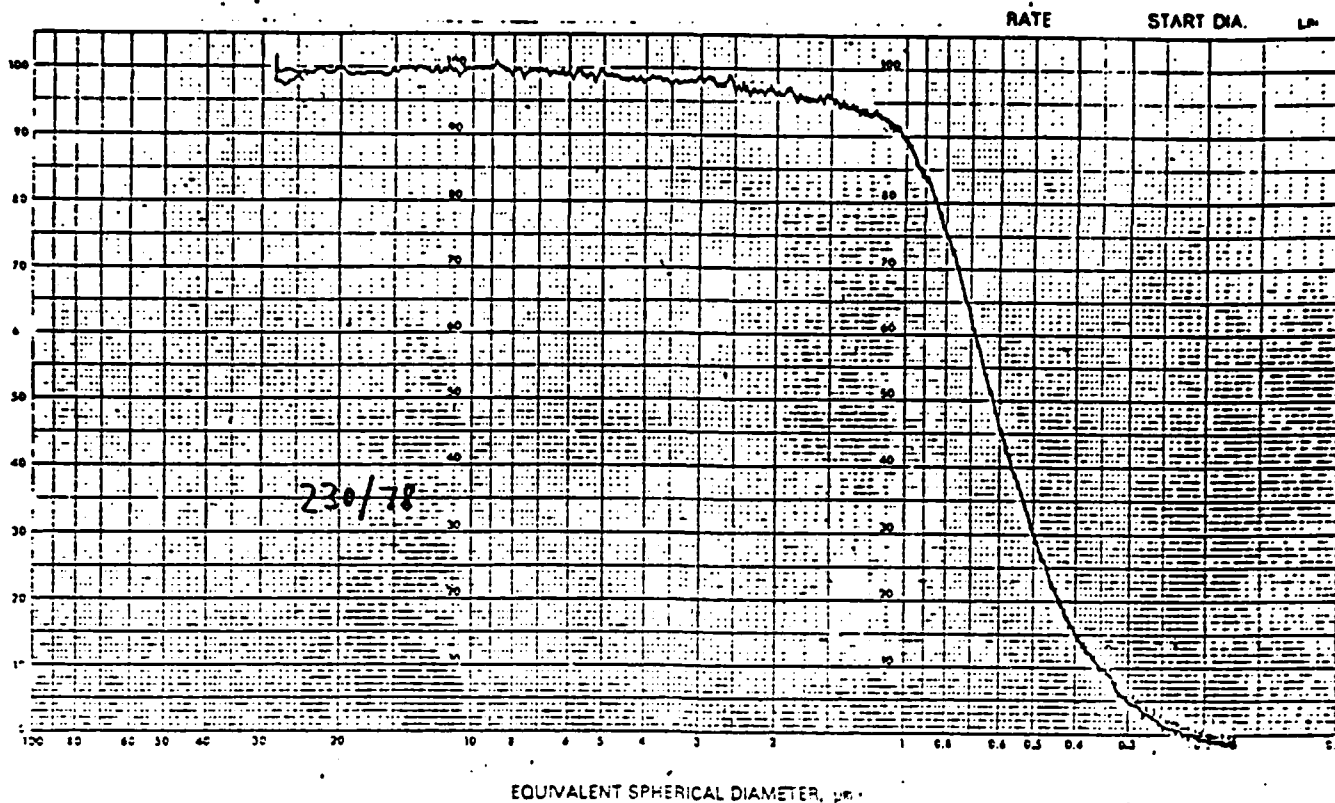
Following the conclusion of the initial investigations, further work will be done to study the influence of doping additives on W grain growth during sintering. Heavy metals with different binder compositions will be made and the effect of different alloying elements, especially Cu, will be tested.

The influence of the sintering atmosphere on the heavy metal properties will be examined closely. Besides pure H_2 , NH_3 , N_2-H_2 mixtures, and Ar atmospheres, as soon as the vacuum furnace is finished it should be possible to sinter under vacuum.

Supplementary investigations, especially concerning the adhesion between the binder and the W grains, and perhaps attempts to improve wettability, are planned.

L i t e r a t u r e

1. E.C.Green, D.J.Jones,
W.R.Wilkins Iron Steele Inst.; Spec.
Rep. 58 (1956) 253
2. R.Kieffer, K.Sedlatschek Planseeber. f. Pulvermet.
5 (1957) 104
3. F. Holtz, R. Thyne Rep. Armour Res. Found.;
Chicago 1969
4. A.J.Davis, D.J.Jones Engl. Pat. 1.172,754-56
(1968)
5. E.I.Larsen, R.H.Krock I. Electrochem. Soc. 108
(1961) 284
6. R.H.Krock, L.A.Shepard Trans. Met. Soc. AIME
227 (1963) 1127
7. R.Minakova, A.Pilyankovich, Poroshkovaya Met. 5 (1968)
O.Teodorovich, I.Frantsevich 73
8. G.Petzow, W.J.Huppmann Z. Metallk. 67 (1976) 571
9. A.R.Poster Powder Met. 2 (1962) 301
10. E.Ariel, J.Barta, D.Brandon Powder Met. Int. 5 (1970) 3
11. J.L.Chermant, M.Coster, Prakt. Metallogr. Sonderb.
P.Dujardin 8 (1978) 192
12. G.Jangg, R.Kieffer, Planseeber. f. Pulvermet.
B.Childeric, E.Ertl 22 (1974) 15

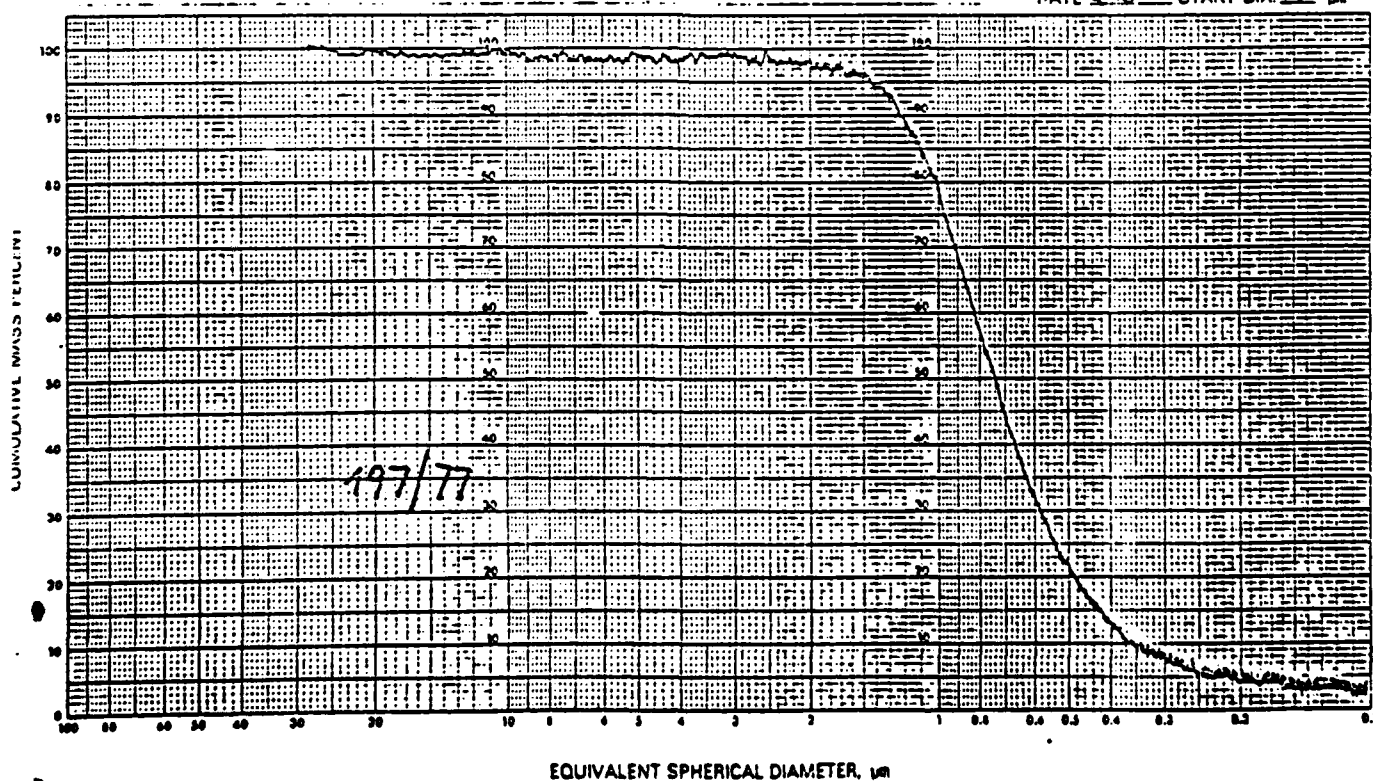


m micromeritics
instrument corporation

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION 197/77 W.B.V. 1/500 4.5-1.25 kg 2.969
 Density 1.013 g/cc LIQUID 200/77 Density 0.8119 g/cc Viscosity 6.917 cp
 Preparation 6.1 200/77 4.5 1.25

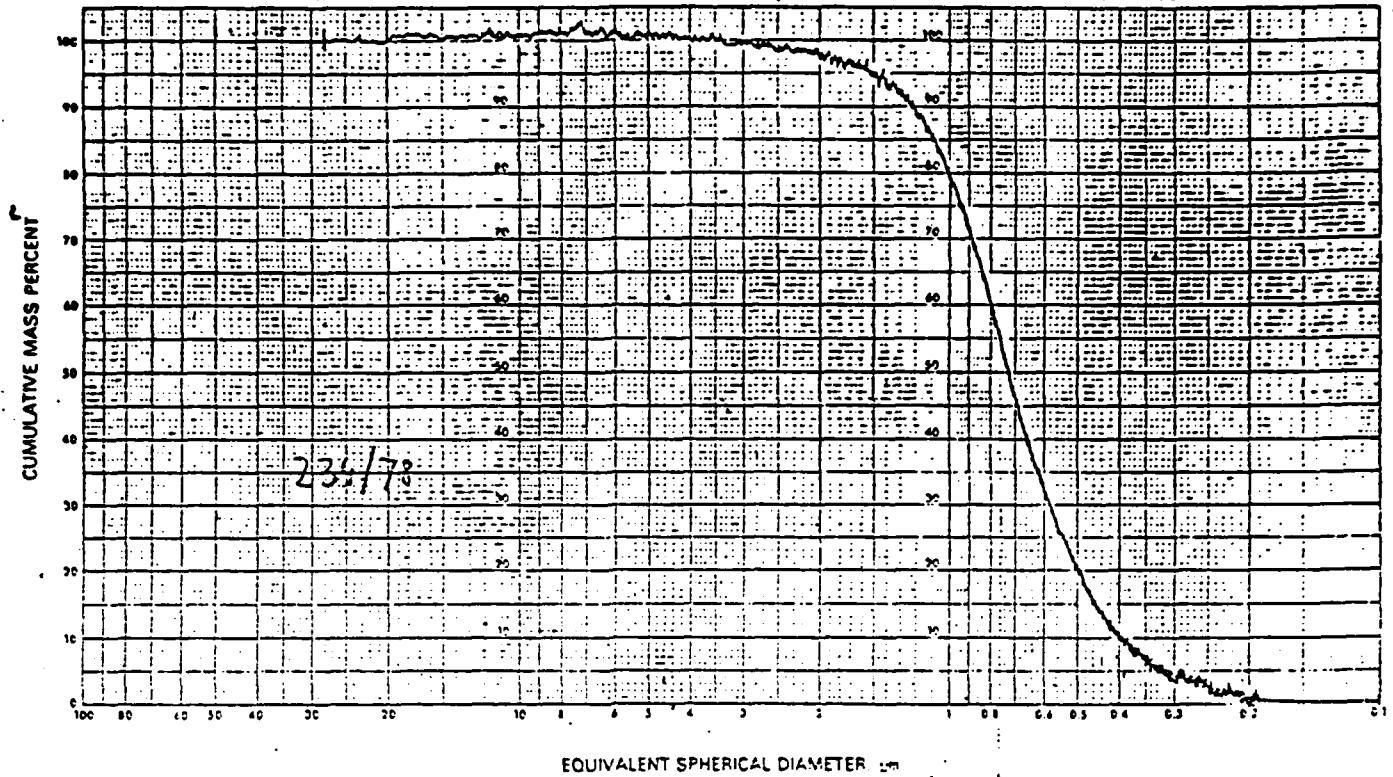
DATE 12/10
 BY 72
 TEMPERATURE 33 °C
 RATE 213 START DIA. 21 μm



m micromeritics

Density 19.3 g/cc LIQUID SEDOSPERS E Density 0.819 g/cc Viscosity 7,600 cp
Preparation 60' dragomeric L + 45' US

BY RA
TEMPERATURE 30 °C
RATE 192 START DIA 72 μ m



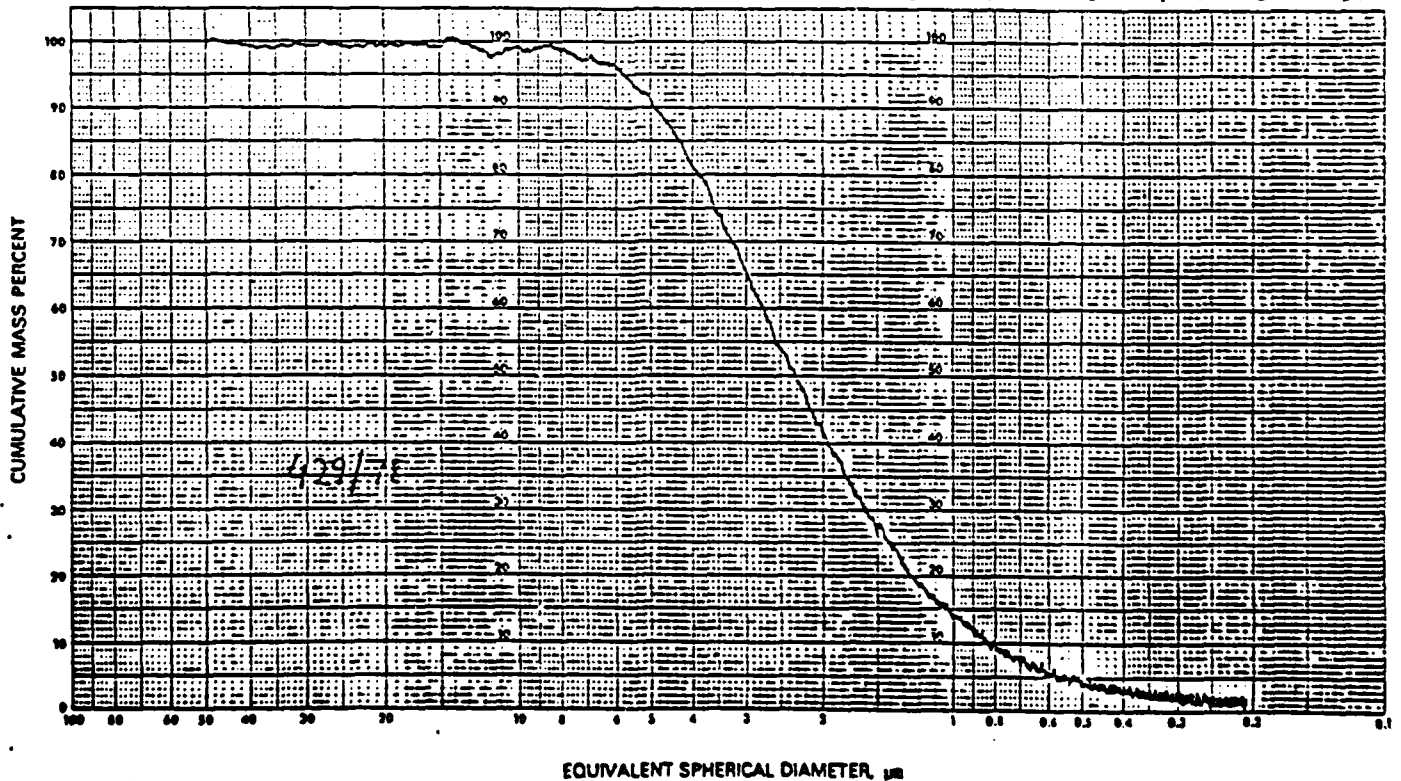
m micromeritics

SAMPLE IDENTIFICATION 429/70 WB / FSS KG = 3.16 μ

Density 19.3 g/cc LIQUID SEDOSPERS H-13 Density g/cc Viscosity cp

Preparation 60' dragomeric L + 15' US

DATE 78-11-07
BY RA
TEMPERATURE 33 °C
RATE 629 START DIA 50 μ m

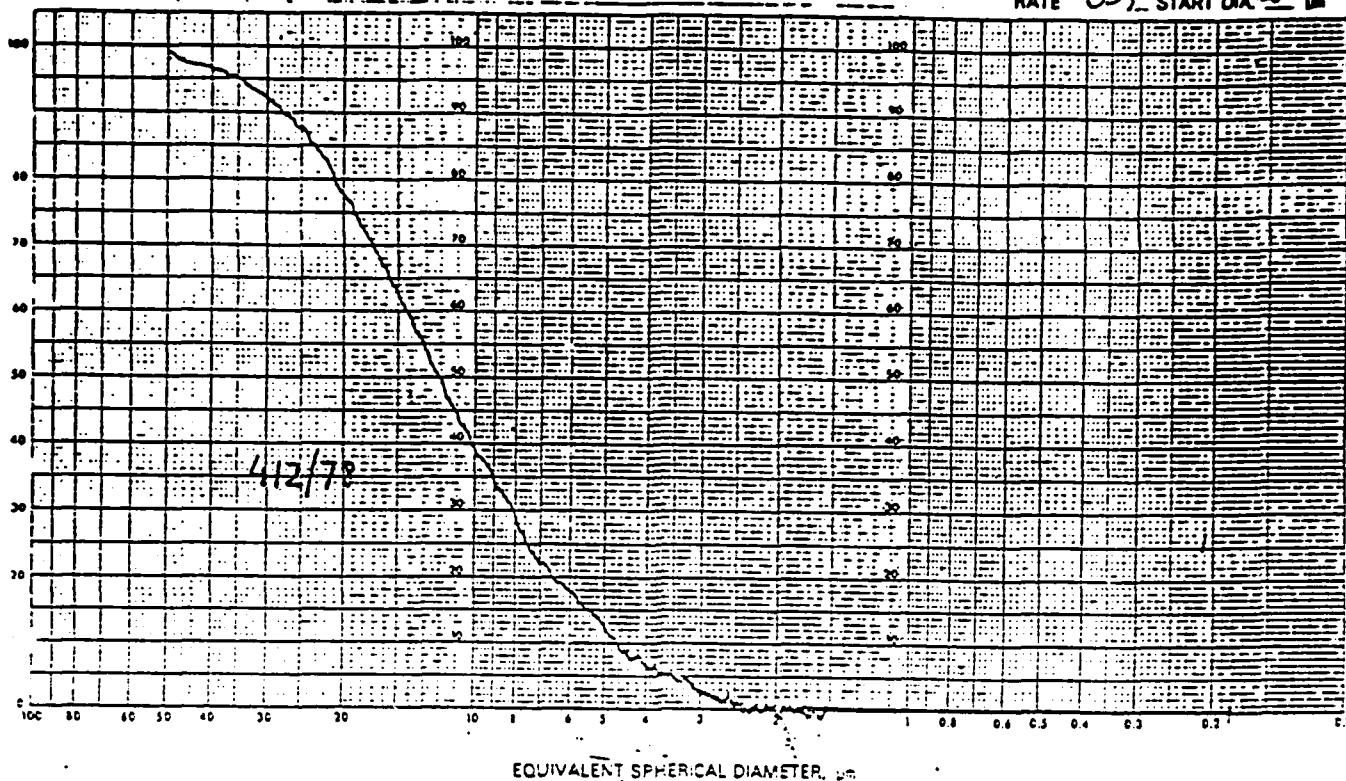


m micromeritics
instrument corporation

Preparation

60' dia agglomerant + 15' WS

TEMPERATURE 32 °C

RATE 65% START DIA 50 μ m

micromeritics

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION 503/79 WB (V)

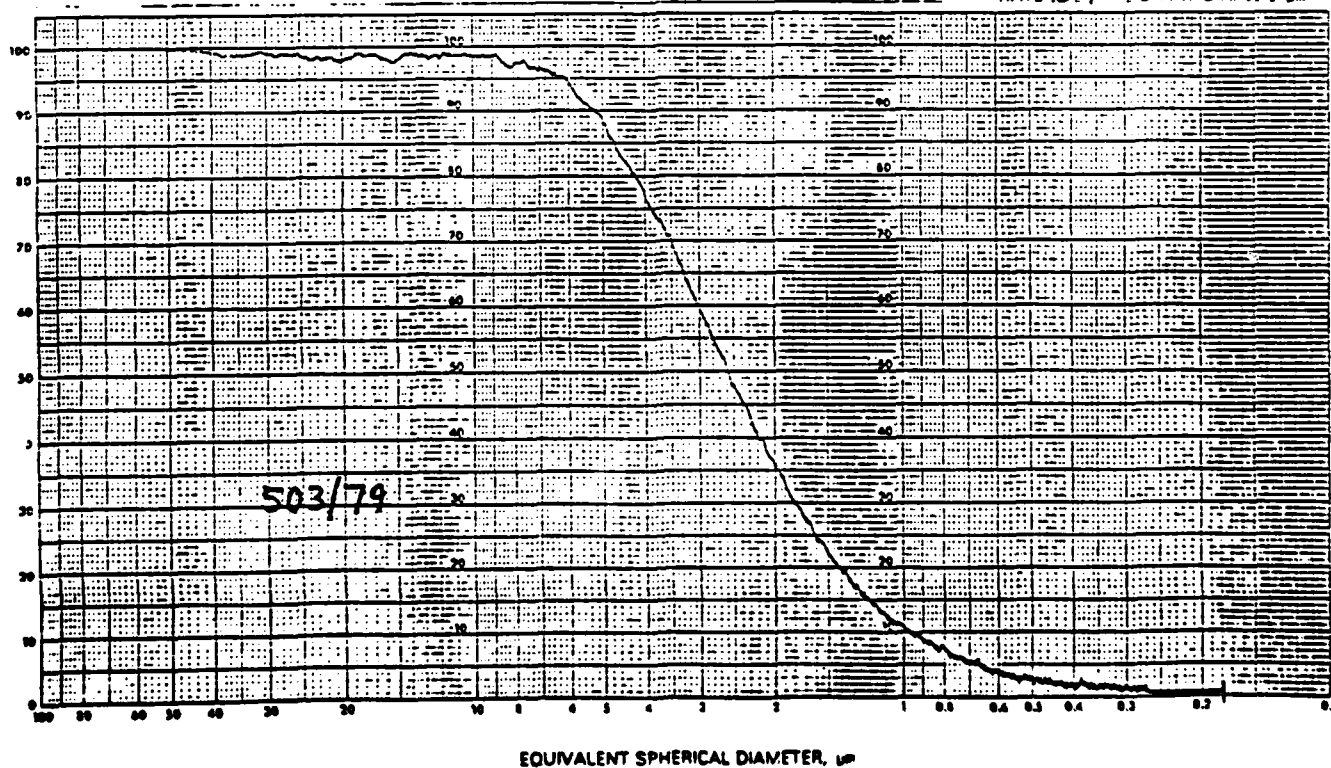
DATE 79-04-05

Density 1.91 g/cc LIQUID DISPENSE H-13 Density g/cc Viscosity cp

BY PH

Preparation 60' dia agglomerant + 15' WS

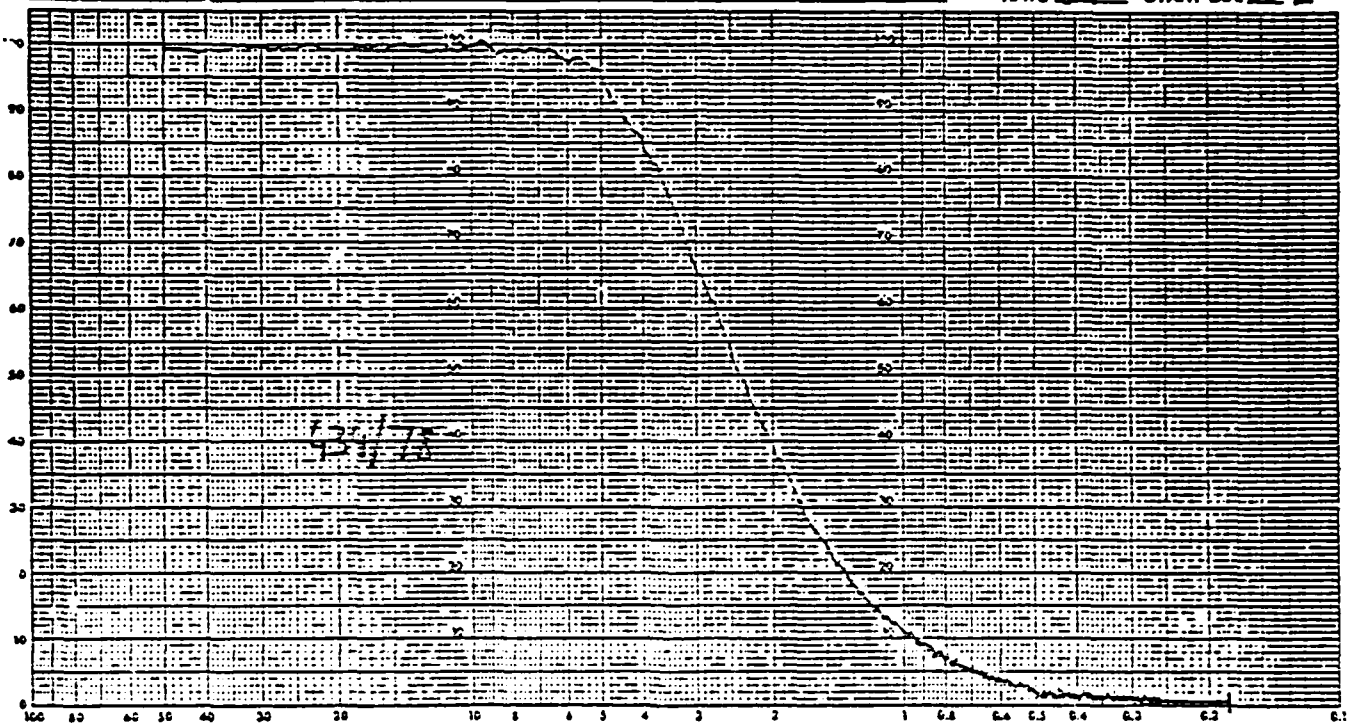
TEMPERATURE 30 °C

RATE 50% START DIA 50 μ m
 micromeritics
instrument corporation

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION 434/72 WB ① / FSS K9-3,13,
 Density 19.3 g/cc LIQUID Spicover 7-13 Density _____ g/cc Viscosity _____ cp
 Preparation 60' dragline material + 15' US

DATE 72-11-27
 BY RA
 TEMPERATURE 51 °C
 RATE 637 START DIA. 50 μ



EQUIVALENT SPHERICAL DIAMETER, μ